TECHNOLOGY DEPT.

PUBLIC LIBRARY
FEB 19 1944

# JOURNAL OF THE CHEMICAL SOCIETY

DECEMBER, 1943

***PATRON:***
HIS MAJESTY THE KING

***President:***
W. H. MILLS, M.A., Sc.D., F.R.S.

***Vice-Presidents***
who have filled the office of President:

F. G. DONNAN, C.B.E., D.Sc., LL.D., F.R.S.
PERCY F. FRANKLAND, C.B.E., D.Sc., LL.D., F.R.S.
SIR ROBERT ROBINSON, M.A., D.Sc., LL.D., F.R.S.
N. V. SIDGWICK, C.B.E., D.Sc., LL.D., F.R.S.
W. P. WYNNE, D.Sc., M.A., F.R.S.

***Vice-Presidents:***

F. H. CARR, C.B.E., D.Sc., F.I.C.
SIR ALFRED EGERTON, M.A., F.R.S.
A. FINDLAY, M.A., D.Sc., Ph.D., F.I.C.
C. S. GIBSON, O.B.E., M.A., Sc.D., F.R.S.
W. N. HAWORTH, D.Sc., Ph.D., F.R.S.
C. K. INGOLD, D.Sc., F.R.S., F.I.C.

***Treasurer:***
F. P. DUNN, B.Sc., F.I.C.

***Secretaries:***

C. W. DAVIES, D.Sc., F.I.C.
G. M. BENNETT, M.A., Sc.D., Ph.D., F.I.C.
W. WARDLAW, D.Sc., F.I.C.

***Ordinary Members of Council:***

J. W. BAKER, D.Sc., Ph.D., F.I.C.
J. W. COOK, D.Sc., Ph.D., F.R.S.
H. J. T. ELLINGHAM, B.Sc., Ph.D., F.I.C.
H. J. EMELÉUS, D.Sc., A.R.C.S.
F. FAIRBROTHER, D.Sc.
J. J. FOX, C.B., O.B.E., D.Sc., F.R.S., F.I.C.
J. M. GULLAND, M.A., D.Sc., Ph.D.
G. S. HARTLEY, D.Sc.
R. D. HAWORTH, D.Sc., Ph.D., F.I.C.
D. J. G. IVES, Ph.D., A.I.C.
F. B. KIPPING, M.A., Ph.D.
E. B. MAXTED, D.Sc., Ph.D., F.I.C.
R. A. MORTON, D.Sc., Ph.D., F.I.C.
E. H. RODD, D.Sc., A.C.G.I., F.I.C.
J. D. M. ROSS, M.B.E., M.A., D.Sc.
B. C. SAUNDERS, M.A., B.Sc., Ph.D.
J. C. SMITH, M.A., M.Sc., Ph.D., D.Sc.
G. B. B. M. SUTHERLAND, M.A., B.Sc., Ph.D.
H. W. THOMPSON, M.A., B.Sc., Ph.D.
W. H. J. VERNON, D.Sc., Ph.D., F.I.C.
H. B. WATSON, D.Sc., Ph.D., F.I.C.

***Ex-Officio Members of Council:***

T. A. HENRY, D.Sc. (*Chairman of the Joint Library Committee*).
L. H. LAMPITT, D.Sc., F.I.C. (*Chairman of the Chemical Council and of the Bureau of Chemical and Physiological Abstracts*).
T. S. MOORE, M.A., B.Sc. (*Chairman of the Publication Committee*).

***General Secretary:***
S. E. CARR, F.C.I.S.

***Acting Librarian:***
A. E. CUMMINS.

*Telephone Numbers:* Office, Regent 6322; Library, Regent 1342.

London: THE CHEMICAL SOCIETY, BURLINGTON HOUSE, W.1

***Committee of Publication:***

*Chairman:* T. S. Moore, M.A., B.Sc.

N. K. Adam, M.A., Sc.D., F.R.S.
A. J. Allmand, M.C., D.Sc., F.R.S.
R. P. Bell, M.A., B.Sc.
G. M. Bennett, M.A., Sc.D.
E. J. Bowen, M.A., F.R.S.
H. V. A. Briscoe, D.Sc., F.I.C.
J. E. Coates, O.B.E., D.Sc., F.I.C.
J. W. Cook, D.Sc., F.R.S.
C. W. Davies, D.Sc., F.I.C.
F. P. Dunn, B.Sc., F.I.C.
H. J. Emeléus, D.Sc., A.R.C.S.
W. E. Garner, D.Sc., F.R.S.
J. M. Gulland, M.A., D.Sc., Ph.D.
C. R. Harington, M.A., Ph.D., F.R.S.
G. S. Hartley, D.Sc.
R. D. Haworth, D.Sc., Ph.D.
I. M. Heilbron, D.S.O., D.Sc., F.R.S.
T. A. Henry, D.Sc.
D. H. Hey, Ph.D., D.Sc., F.I.C.
E. L. Hirst, M.A., D.Sc., F.R.S.
E. D. Hughes, D.Sc., Ph.D., F.I.C.
J. Kenyon, D.Sc., F.R.S.
F. G. Mann, D.Sc., F.I.C.
H. W. Melville, Ph.D., D.Sc., F.R.S.
W. H. Mills, M.A., Sc.D., F.R.S.
A. Robertson, M.A., Ph.D., F.R.S.
J. L. Simonsen, D.Sc., F.R.S., F.I.C.
J. C. Smith, M.A., M.Sc., Ph.D., D.Sc.
S. Sugden, D.Sc., F.R.S.
A. R. Todd, D.Sc., D.Phil., F.R.S.
W. Wardlaw, D.Sc., F.I.C.

***Editor:*** Clarence Smith, D.Sc.

***Assistant Editor:*** A. D. Mitchell, D.Sc.

***Indexer:*** Margaret Le Pla, B.Sc.



**Subscription Rate, £3.15.0 per annum, post free**


The Chemical Society was founded in 1841 and received a Royal Charter in 1848.

The main function of the Society is to foster original research in Chemistry and to facilitate the discussion and dissemination of new knowledge in all branches of the science.

## FELLOWSHIP

Fellowship of the Chemical Society is open to men and women of all nationalities who are interested in Chemistry and wish to keep in touch with its advances. Fellows are elected by the Council.

## PRIVILEGES

Fellows who pay the annual subscription of £3 have the following privileges

1. To receive any three of the following publications of the Society without extra charge:
*Journal of the Chemical Society.*
*British Chemical and Physiological Abstracts "AI," "AII," or "AIII."*
*Annual Reports on the Progress of Chemistry.*
*Reprints of Lectures published in the Journal.*

One copy of the Abstracts "A" Index and of Abstracts C (Analysis and Apparatus) are supplied to Fellows receiving one or more sections of the Abstracts. Publications in excess of the three allowed can be purchased at schedule prices.

2. To consult and borrow the books in the Library (44,000 volumes).

3. To attend meetings of the Society both in London and outside London, and to introduce two guests thereto.

4. To apply for research grants.

5. To submit original papers for publication in the *Journal.*

Fellows under the age of 25 have the option of paying half the annual subscription (£1 10s.) and receiving until the end of the year in which they reach that age:

The *Annual Reports on the Progress of Chemistry*, and either the *Journal of the Chemical Society* or two sections of *British Chemical and Physiological Abstracts A.*

Such Fellows receive no other publications of the Society, but enjoy all the other privileges accorded to those paying the full annual subscription.

## PUBLICATIONS

(*a*) *The Journal of the Chemical Society*, which is published monthly, contains the results of investigation which cover the whole field of pure chemistry.

(*b*) *British Chemical and Physiological Abstracts.*

The Society collaborates with the Society of Chemical Industry, the Physiological Society, and the Biochemical Society in maintaining the Bureau of Chemical and Physiological Abstracts, which issues every month abstracts of papers dealing with all branches of pure and applied chemistry and physiology published in all parts of the world.

*British Chemical and Physiological Abstracts A* is divided into three sections: AI, General, Physical and Inorganic Chemistry; AII, Organic Chemistry; AIII, Physiology and Biochemistry, including Anatomy.

(*c*) *Annual Reports on the Progress of Chemistry.* These reports, written by experts, summarise the important new advances in pure chemistry and related subjects.

## LIBRARY

The extensive reference and lending library of the Chemical Society contains over 45,000 volumes dealing with every aspect of Chemistry and with many branches of related sciences. The Library is open on Monday to Friday from 10 a.m. to 5 p.m., and from 10 a.m. to 1 p.m. on Saturdays.

## MEETINGS

(*a*) *In London.*

Scientific Meetings of the Society are held usually on the first and third Thursdays of each month from October to June at Burlington House, at which papers dealing with original work are read and discussed, organised discussions on subjects of current interest are arranged, and lectures by eminent British and foreign chemists are delivered.

(*b*) *Outside London.*

Scientific Meetings and lectures are also held outside London, and form an important part of the activities of the Society in the Provinces.

## RESEARCH FUND

A Research Fund is available for the assistance of chemical research, and sums amounting annually to about £700 are granted for this purpose. Application for grants must be made on the appropriate form, which may be obtained from the General Secretary.

---

Forms of Application for Fellowship can be obtained from The General Secretary, The Chemical Society, Burlington House, Piccadilly, London, W.1.

***CHINA CLAYS (Kaolin)***
***BALL CLAY (Argile)***
***CORNWALL STONE (China Stone)***
***FELSPAR · KALYTES (Barytes Substitute)***
***ALUMINIUM SILICATE (Talc Substitute)***
***BENTONITE (and British Substitutes)***
***TALC (and British Substitutes)***
***QUARTZ SANDS***
***REFRACTORY CLAYS, BRICKS, TILES, etc. and other products.***

*for use in the manufacture of*

Paper
Textiles
Earthenware
Porcelain
Refractories
Crucibles
Furnace Linings
Furnace Moulds
Insulators
Cement
Stoneware
Glass
Fuses
Paints
Enamels
Rubber Goods
Cables
Ultramarine
Inks
Insecticides
Matches
Fireworks
Medicines
Poultices
Cosmetics
Polishes
Roofing Felts
Soaps
etc.

*THERE ARE MANY TYPES OF CHINA CLAY, BALL CLAY, etc., EACH HAVING ITS OWN PECULIARITIES. THEY DIFFER IN ANALYSES, PARTICLE SIZE, COLOUR, SUSPENSION, etc. They can be supplied in bulk or in finest powder form.*

- ***Let us know what you are seeking***

*and we will make recommendations and supply copious samples for tests.*

*Our British substitutes for foreign minerals are in daily increasing demand.*

- *A few of our SPECIAL KAOLINS supplied in the finest powder form :*

**STOCKALITE**
**DEVOLITE**
**COLWHITE**
**SPESWHITE**
**SUPREME**

- *TALC SUBSTITUTES :* **TAKOLIN · TAKOLITE, Etc.**
- *BARYTES SUBSTITUTE :* **KALYTES**

**PRODUCERS :**

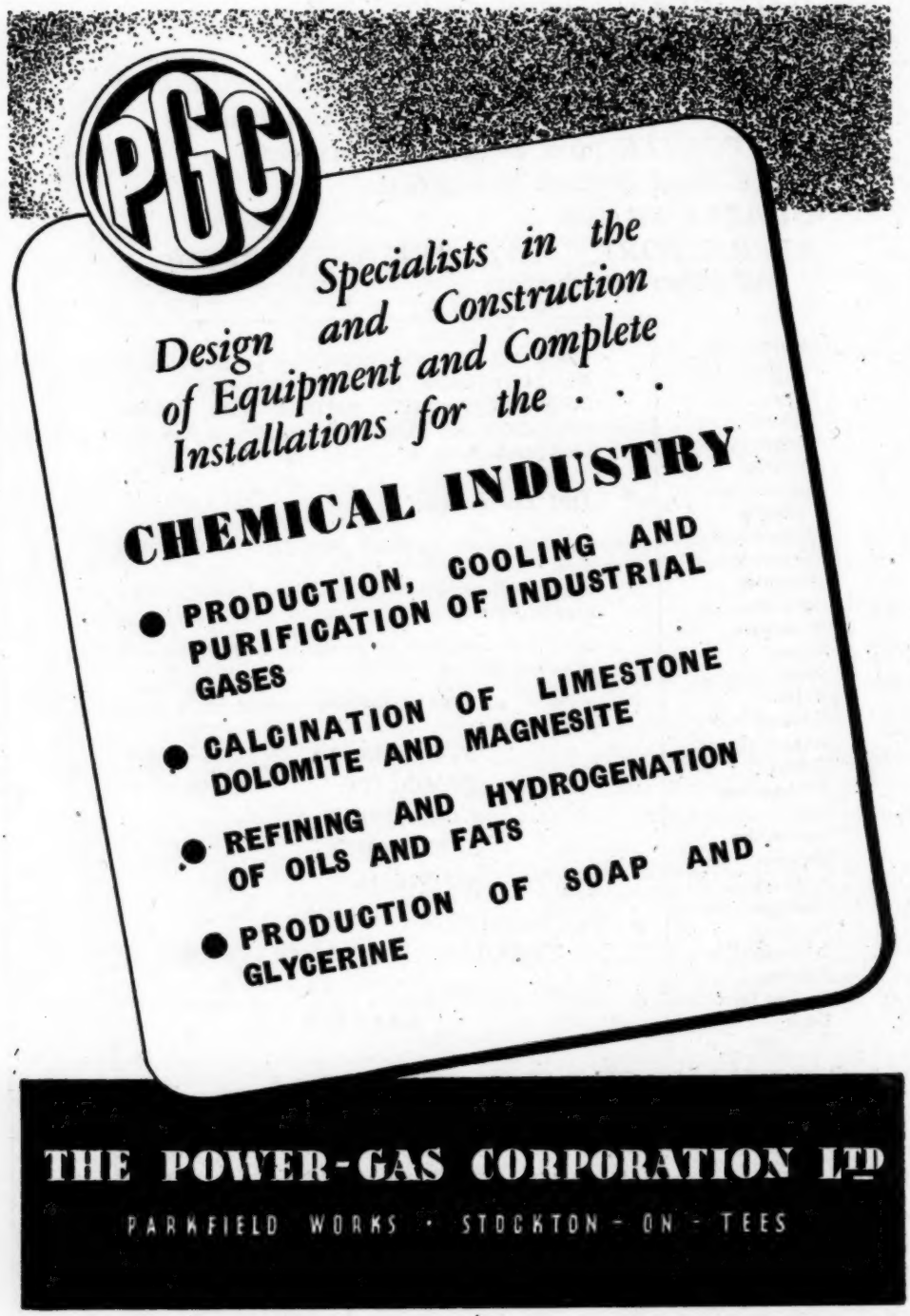
**ENGLISH CLAYS LOVERING POCHIN & CO. LTD.**

*HEAD OFFICE, MINES and MILLS at*

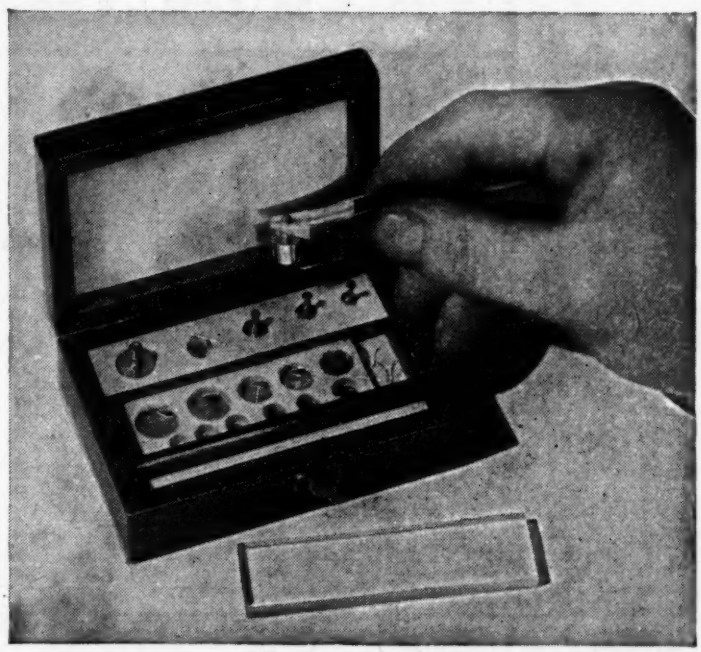
**ST. AUSTELL CORNWALL**

*Offices also at London, Stoke, Manchester, Newcastle, Edinburgh, etc.*
*Depots and Stores in many parts of the country.*

**Telegrams : Universal, St. Austell.** **'Phone : 482 St. Austell.**


PGC
Specialists in the Design and Construction of Equipment and Complete Installations for the . . .
CHEMICAL INDUSTRY
● PRODUCTION, COOLING AND PURIFICATION OF INDUSTRIAL GASES
● CALCINATION OF LIMESTONE DOLOMITE AND MAGNESITE
● REFINING AND HYDROGENATION OF OILS AND FATS
● PRODUCTION OF SOAP AND GLYCERINE
THE POWER-GAS CORPORATION LTD
PARKFIELD WORKS · STOCKTON-ON-TEES

THE FINEST *Quality* IN THE WORLD



BRITISH PRECISION BALANCES & WEIGHTS

- CHEMICAL BALANCES
- ASSAY BALANCES
- MICRO-CHEMICAL BALANCES
- BULLION BALANCES
- PRECISION WEIGHTS

*Please request detailed list*

L. OERTLING LTD.
110 GLOUCESTER PLACE,
PORTMAN SQ., LONDON, W.1

Oertling
TO HOLD IN LONDON BEFORE THAT

TAS/OR. 217

# ALDOL

## $CH_3.CH(OH).CH_2.CHO$

**SPECIFICATION AND PROPERTIES:**

Nature - - Viscous, almost colourless liquid.
Specific Gravity- Not below 1.10 @ 15/15° C.
Purity - - Not less than 90% aldehyde (calculated as aldol).

**SUGGESTED USES:**
1. Manufacture of synthetic resins.
2. Manufacture of B-hydroxy-butanol.
3. Manufacture of aldehyde-amines.

**ENQUIRIES:** BRITISH INDUSTRIAL SOLVENTS LTD.
*Welbeck House, Downs Side, Belmont, Surrey. Telephone: Vigilant* 0133.

**LESSING CONTACT RINGS**
for packing
**Fractionating Columns**
**Absorbers**
**Catalyst Vessels**
**Combustion Tubes**

*MADE IN*
**All Metals**
**Porcelain**
**Chemical Stoneware**
**Glass Carbon**

**Sizes from $\frac{1}{8}$" × $\frac{1}{8}$" to 4" × 4"**

*Tell us your problems*

**THE HYDRONYL SYNDICATE LTD.**
**14 Gloucester Road**
**London, S.W.7**

**The Royal Institute of Chemistry of Great Britain and Ireland**
Founded 1877. Incorporated by Royal Charter, 1885.

**APPOINTMENTS REGISTER.**—A Register of Chemists (Fellows, Associates and Senior Registered Students) who are available for appointments, or who are seeking to improve their positions, is kept at the office of the Institute. The facilities afforded by this Register are available (free) to Companies and Firms requiring the services of Chemists, and to Universities, Colleges and Technical Schools requiring Teachers of Chemistry and Technology. A List of Laboratory Assistants is also available.

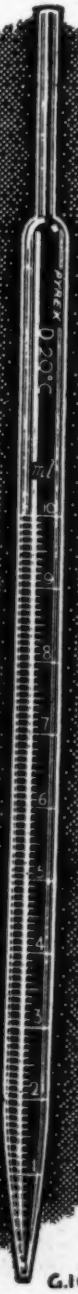
Particulars of the Regulations and Examinations of the Institute can be obtained (free) on application to the Registrar.

*All communications to be addressed to*

**The Registrar,**
**The Royal Institute of Chemistry,**
**30 Russell Sq., London, W.C.1**

PYREX
REGD. TRADE MARK BRAND

Graduated Glassware




By specifying "PYREX Brand" when ordering Graduated Glassware you are assured of obtaining strong serviceable glassware, with division lines and numerals etched clearly and precisely, for easy reading.

For everyday laboratory work PYREX Brand Glassware is graduated to N. P. L. class B standard, but for more meticulous analysis or intricate research work, N. P. L. class A can be supplied at the appropriate extra costs.

*PYREX Brand Graduated Glassware is supplied only through Laboratory Furnishers, but illustrated catalogue and two free copies of our Chemist's Notebook will be sent direct on application to us.*

**Ask for PYREX Brand and see that you get it!**

JAMES A. JOBLING & CO. LTD.
WEAR GLASS WORKS
SUNDERLAND.

G.10.A.

# Some 'GENATOSAN' FINE CHEMICALS

GEN

**PHLOROGLUCINOL.**

**Substantial reductions in price have recently been made.**

**NICOTINIC ACID AMIDE.**

**A recent addition to our range. Of medicinal interest.**

**β-NAPHTHYL HYDRAZINE Hydrochloride.**

**A valuable reagent in the detection and estimation of aldehydes and ketones.**

**We also manufacture:**

**Hydrazine salts**
**Rubidium salts**
**Methyl and Ethyl Urea**
**Urethane**
**Nicotinic acid**
**Uric acid**
**Allantoin**
**Alloxantin**

*and invite enquiries for these and allied materials.*

Buyers are reminded that our ability to contract for deliveries of certain materials is contingent on purchasers satisfying the various Raw Material Controls as to the essentiality of their needs.

**GENATOSAN LTD., LOUGHBOROUGH, LEICS.**

**Claisen Reactions—**

It has been shown that the condensation of compounds containing the keto-methylene group with various reactants may often be carried out to advantage in the absence of an alcoholic solvent using Sodium Alkoxides

**ANHYDROUS SODIUM METHOXIDE $CH_3ONa$**

is a convenient and practical condensing agent for many such syntheses. It is therefore offered for research and development purposes as a finely divided free flowing white powder, free from Methyl Alcohol and Sodium Hydroxide.

References:
Hauser & Hudson. Organic Reactions, **1942**, 278.
Bachman, Cole & Wilds, J.A.C.S. **62**, 835.
Fisher & McElvain, J.A.C.S. **56**, 1766.
Komppa. Ann. **368**, 137.

Packings: 25 g. Ampoules
500 g. Bottles

**Made and Supplied by**
HERTS PHARMACEUTICALS LIMITED
Fine Chemicals Section
WELWYN GARDEN CITY, HERTS
Telephone: Welwyn Garden 3333–6

WRITE FOR SAMPLES and TECHNICAL INFORMATION..

PURE CRYSTAL **ALUM**
OF UNVARYING COMPOSITION & UNRIVALLED PURITY

**SULPHATE OF ALUMINA**
ALL GRADES SUPPLIED

**"ALUMINOFERRIC"** REGD
THE CHEAPEST FORM OF SULPHATE OF ALUMINA

**ACTIVATED ALUMINA**
ADSORBENT AND CATALYST

**SODIUM ALUMINATE**
HIGHEST QUALITY · FOR WATER SOFTENING

**"NEOSYL"** REGD (AMORPHOUS SILICA)
UNIQUE LIGHTNESS & FINENESS

**"TYPHOX"** AND TITANIUM POTASSIUM OXALATE
IDEAL MORDANTS FOR LEATHER DYEING.

**TITANOUS SULPHATE**
A MOST POWERFUL & ECONOMICAL STRIPPING AGENT

**PETER SPENCE & SONS LTD**
NATIONAL BUILDINGS · MANCHESTER 3
LONDON OFFICE: 4 HANGER GREEN · EALING · W5

G.1

THE *NEW* B.T.L.

**METAL FILTER PUMP**

- High Performance
- Simple Construction
- Nickel-plated Finish
- Replaceable Jet
- May be operated by steam or compressed air for low vacuum

**Price 7/6 each** **81/- per doz.**

*All Enquiries and Orders to Dept. 1/6*

**BAIRD & TATLOCK (LONDON) LTD.**

*Manufacturers of Laboratory Equipment*

14-17 ST. CROSS STREET, LONDON, E.C.1

TO
MEDICAL OFFICERS
NURSES
FIRST AID POSTS

**WOUNDS, BURNS** etc.
***HEAL RAPIDLY*** *and*
***WILL NOT TURN SEPTIC***
*IF TREATED WITH*

# ANTIPEOL CUTANEOUS VACCINE OINTMENT

BECAUSE one or other or all of the three races of germs, Streptococci, Staphylococci, and B. pyocyaneus are found in every skin infection common to this country, and ANTIPEOL OINTMENT contains the *antibodies* (antivirus) of these germs. Healing is expedited by the proved ingredients of the ointment, and septic development is stopped or prevented by its antivirus sterile vaccine filtrates. ANTIPEOL OINTMENT is unsurpassed for BURNS and SCALDS, for it is microbicide and non-adhesive, and dressings do not require to be changed every day.

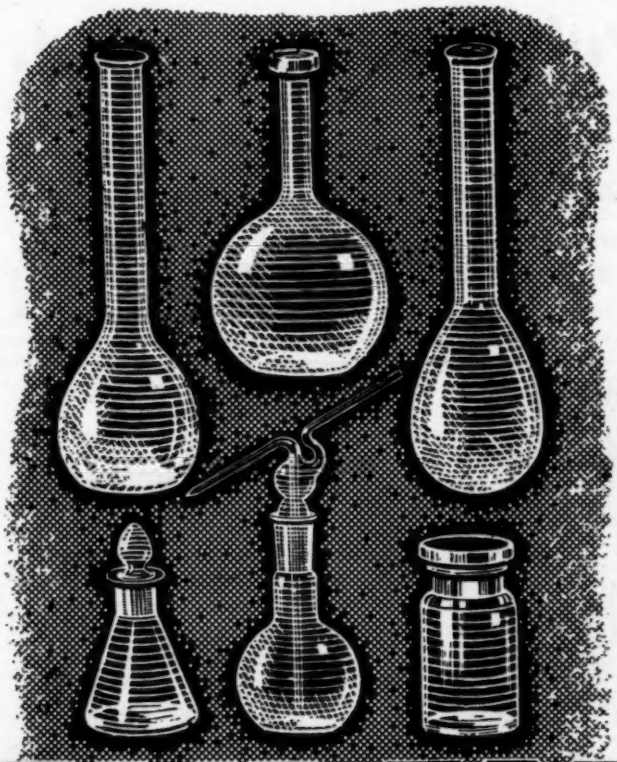
## RHINO-ANTIPEOL

affords rapid relief of COMMON COLDS, INFLUENZA, AND CATARRH. Containing the antibodies of the germs common to infections of the nose and pharynx (Staphylococci, Streptococci, B. pyocyaneus, pneumococci, pneumobacilli, enterococci, M. catarrhalis, B. Pfeiffer), Rhino-Antipeol is not just a palliative, but is a remover of the *cause* of the infection. During epidemics it is the ideal preventive of microbic development.

## OPHTHALMO-ANTIPEOL

is a semi-fluid ointment, more convenient than the ordinary Antipeol ointment for ocular infections and lesions. Eyes affected by smoke and dust are soothed almost immediately by the application of Ophthalmo-Antipeol, and the antivirus prevents germs from developing.

**Clinical Samples on request from**
**MEDICO-BIOLOGICAL LABORATORIES LTD.**
**CARGREEN ROAD, SOUTH NORWOOD, LONDON, S.E.25**



# PYREX

REGD. TRADE MARK. BRAND.

## SCIENTIFIC GLASSWARE

### The high-light of Craftsmanship

*PYREX Brand Scientific Glassware is supplied only through Laboratory Furnishers, but illustrated catalogue and two free copies of our Chemist's Notebook will be sent direct on application to us.*

For many years, much thought and the close application of the craftsman's skill, has been given to the evolution of glassware that would meet the demands of the scientist in his specialized research work.

With the advent of PYREX Brand Scientific Glassware this need has been adequately met, and in the laboratory and the dispensary alike, this remarkable glassware is found to be both safe and reliable. Its low co-efficient of expansion (·0000032) makes it almost completely immune from the effects of sudden thermal changes.

That is why it has been possible to make PYREX Brand Scientific Glassware of more robust build than that of ordinary glass, thus effectively reducing the risk of breakage resulting from continuous everyday handling.

**Ask for PYREX Brand and see that you get it!**

James A. Jobling & Co. Ltd.

Wear Glass Works,

SUNDERLAND.

T.29.C.

# The Crack Pulverising Mills Ltd.

**GRINDERS TO THE TRADE FOR**

**DRUGS, GUMS, SPICES and CHEMICALS**

**Expert Staff available for Reconditioning of Gums, Drugs, etc., Damaged by Fire or Water.**

*Address all communications to—*

**"THE HAWTHORNS," LEATHERHEAD ROAD, BOOKHAM (SURREY)**

**Works: Tannery Lane, Send, nr. Woking (Surrey).** **Phone: BOOKHAM 2748**

## VITREOSIL

**ALWAYS RELIABLE**
**READILY OBTAINABLE**

No user need fear shortage of supplies of VITREOSIL, pure fused silica. A large variety of acid and heat-proof ware is available for the laboratory or the works.

**THE THERMAL SYNDICATE LTD.**
**Head Office: Wallsend, Northumberland**
London Depot: 12–14 Old Pye St., Westminster, S.W.1
*Established over 30 years*

# SCIENTIFIC BOOKS

**Books on the *Chemical* and Allied Sciences supplied from stock, or obtained to order.**

**Please state interests when writing.**

***Foreign Books* not in stock obtained under Licence.**

**A wide selection of *Second-hand Books* may be seen at *140 Gower Street*.**

## H. K. LEWIS & Co. Ltd.

**136 GOWER STREET, LONDON, W.C.1**

*Telegrams: 'Publicavit, Westcent, London.'* *Telephone: EUSton 4282 (5 lines).*

*Sole Sales Representatives:—*

## WHATMAN *High Grade* FILTER PAPERS

*H. REEVE ANGEL & Co., Ltd.*
*9 Bridewell Pl., London, E.C.4*

**ETHER-TREATED**
**EXTRACTION THIMBLES**
**(SEAMLESS)**

These thimbles have been treated with ether to make them as fat-free as is commercially possible. Very popular for use in Soxhlet apparatus. Supplied in single or double thickness.

**FROM ALL LABORATORY FURNISHERS.** **Specify "WHATMAN."**

# CONTENTS.

## PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

### General, Physical, and Inorganic.


PAGE

THE TILDEN LECTURE.—Recent Advances in the Theory of Reaction Kinetics in Solution.
By R. P. BELL . . . . . 629

169. Physical Properties and Chemical Constitution. Part VIII. Alkyl Chlorides, Bromides, and Iodides.
By ARTHUR I. VOGEL . . . . . 636

170. Transport Numbers of Nitric Acid in Water at 25° from E.M.F. Measurements.
By H. I. STONEHILL . . . . . 647


### Organic.


156. 2 : 4-Diarylpyrroles. Part I. Synthesis of 2 : 4-Diarylpyrroles and 2 : 2′ : 4 : 4′-Tetra-arylazadipyrromethines.
By MAURICE A. THOROLD ROGERS . . . . . 590

157. 2 : 4-Diarylpyrroles. Part II. Methines.
By MAURICE A. THOROLD ROGERS . . . . . 596

158. 2 : 4-Diarylpyrroles. Part III. 3-Amino-2 : 4-diphenylpyrrole.
By MAURICE A. THOROLD ROGERS . . . . . 598

159. Studies in the Sterol Group. Part XLV. Investigation of the Homogeneity of Sitosterol by Oxidation with the Oppenauer Reagent.
By D. H. R. BARTON and E. R. H. JONES . . . . . 599

160. Studies in the Sterol Group. Part XLVI. The Isolation of a New Form of $\Delta^4$-Cholestenone.
By D. H. R. BARTON and E. R. H. JONES . . . . . 602

161. Some Properties of Urea, Biuret, and Triuret.
By R. COLIN HAWORTH and FREDERICK G. MANN . . . . . 603

162. The Preparation and Properties of Certain Poly-sulphanilamide Compounds.
By FREDERICK G. MANN and JAMES WATSON . . . . . 606

163. Dienoestrol.
By G. I. HOBDAY and W. F. SHORT . . . . . 609

164. β-Cholesterol Oxide.
By R. A. BAXTER and F. S. SPRING . . . . . 613

165. Long-chain Acids containing a Quaternary Carbon Atom. Part II.
By N. POLGAR and SIR ROBERT ROBINSON . . . . . 615

166. The Amylolytic Degradation of Starch.
By W. N. HAWORTH, H. KITCHEN, and S. PEAT . . . . . 619

167. The Constitution of Yeast Ribonucleic Acid. Part VI. The Nature of the Carbohydrate Radicals.
By J. MASSON GULLAND and GEOFFREY R. BARKER . . . . . 625

168. Preparation of 2 : 3-Dinitronaphthalene and of 3-Nitro-2-naphthylamine.
By HERBERT H. HODGSON and HAROLD S. TURNER . . . . . 635

171. Aminoacridines : Some Partition and Surface Phenomena.
By ADRIEN ALBERT, REGINALD GOLDACRE, and ERIC HEYMANN . . . . . 651

172. The Diels–Alder Synthesis with 2 : 3-Dimethylquinoxaline. The Reaction between Maleic Anhydride and Anthranil.
By A. SCHÖNBERG and AHMED MOSTAFA . . . . . 654

173. The Complex-formation and Rearrangement of *p*-Hydroxylaminobenzenesulphonamide.
By H. BURTON and N. WALKER . . . . . 656

174. Heterocyclic Nitrogen Compounds. Part I. Derivatives of 7 : 16-Diazanaphthacene.
By H. H. HATT and (MISS) E. F. M. STEPHENSON . . . . . 658

175. Attempts to prepare Optically Active Tervalent Nitrogen Compounds. Part II. 1 : 9-(2′ : 3′ : 4′ : 5′-Tetrahydrophenylene)carbazole.
By ROBERT W. G. PRESTON and S. HORWOOD TUCKER . . . . . 659

NOTES.—Note on the Co-ordination Number of Bivalent Lead.
By R. COLIN HAWORTH and FREDERICK G. MANN . . . . . 661

Preparation of Derivatives of 2 : 2-Dialkyl*cyclo*hexanone.
By ARTHUR J. BIRCH . . . . . 661

# INDEX OF AUTHORS' NAMES.


ALBERT, A., Goldacre, R., and Heymann, E., 651.
Barker, G. R. See Gulland, J. M.
Barton, D. H. R., and Jones, E. R. H., 599, 602.
Baxter, R. A., and Spring, F. S., 613.
Bell, R. P., 629.
Birch, A. J., 661.
Burton, H., and Walker, N., 656.
Goldacre, R. See Albert, A.
Gulland, J. M., and Barker, G. R., 625.
Hatt, H. H., and Stephenson, (Miss) E. F. M., 658.
Haworth, R. C., and Mann, F. G., 603, 661.
Haworth, W. N., Kitchen, H., and Peat, S., 619.
Heymann, E. See Albert, A.
Hobday, G. I., and Short, W. F., 609.
Hodgson, H. H., and Turner, H. S., 635.
Jones, E. R. H. See Barton, D. H. R.
Kitchen, H. See Haworth, W. N.
Mann, F. G., and Watson, J., 606.
Mann, F. G. See also Haworth, R. C.
Mostafa, A. See Schönberg, A.
Peat, S. See Haworth, W. N.
Polgar, N., and Robinson, (Sir) R., 615.
Preston, R. W. G., and Tucker, S. H., 659.
Robinson, (Sir) R. See Polgar, N.
Rogers, M. A. T., 590, 596, 598.
Schönberg, A., and Mostafa, A., 654.
Short, W. F. See Hobday, G. I.
Spring, F. S. See Baxter, R. A.
Stephenson, (Miss) E. F. M. See Hatt, H. H.
Stonehill, H. I., 647.
Tucker, S. H. See Preston, R. W. G.
Turner, H. S. See Hodgson, H. H.
Vogel, A. I., 636.
Walker, N. See Burton, H.
Watson, J. See Mann, F. G.


## ERRATA.

VOL., 1943.

| Page | Line | |
|---|---|---|
| 140 | 8* | *For* " OMe " *read* " 4OMe." |
| 319 | 8 | *After* " sodium sulphide (27·5 g.) " *insert* " and powdered sulphur (7·4 g.)." |

* From bottom.

system, which began at 800—1000° with different materials, lowered both adsorption and reactivity (they nearly disappeared in a coke heated at 1400° for 25 hours). Superficial graphitisation increased these effects. The reactivity increased rapidly with rise of the temperature of gasification in carbon dioxide, but the temperature coefficient of reactivity diminished.

(v) The influence of inorganic constituents on sugar coke, chosen as being of known constitution, rather low reactivity (0·6), and negligible ash content, was studied by impregnation with soluble salts. Reactivity was continuously and greatly raised as the proportion of added soda was increased in stages to 1·4%. Equivalent additions (0·01 g.-mol. of oxide per 100 g. of the coke) of different inorganic substances showed that alkalis and alkaline earths were the most effective in raising this reactivity (*e.g.*, BaO, 13·0; $K_2O$, 3·4). In spite of this increase, the adsorption after the preheating as applied in a carbon dioxide reactivity test was the same for soda coke and baryta coke as for the coke alone. Also, Dent and Cobb had shown that, although sodium carbonate accelerated the approach to equilibrium on passing carbon dioxide over graphite at 800°, yet the equilibrium figure obtained (13·8% of dioxide) was the same. Catalysis was therefore indicated as the cause of the enhanced reactivity.

We record our thanks to the department of Scientific and Industrial Research (Fuel Research Board) for research grants (to G. M. and E. S.), to the suppliers of materials, and to Mr. H. J. Hodsman for advice and assistance throughout in experimental work.

FUEL DEPARTMENT, THE UNIVERSITY OF LEEDS. [*Received, July 5th*, 1943.]

---

# NOTE.

*The Free Energy of Methyl Ether from the Methanol–Methyl Ether Equilibrium* $2MeOH(v.) = Me_2O + H_2O(v.)$. By P. H. GIVEN.

PARKS and HUFFMAN ("The Free Energies of Some Organic Compounds," 1932) calculate, from a single value of the equilibrium constant of the reaction at 623° K. (McKee and Burke, *Ind. Eng. Chem.*, 1923, **15**, 793) and Thomsen's value of the heat of combustion of methyl ether (*Z. physikal. Chem.*, 1905, **52**, 347), that the standard free energy of methyl ether is $\Delta G^0_{298\cdot1} = -26{,}350$ cals. Since 1932 new data have appeared, but the free energy has not been recalculated. Gajendragad, Jatkar, and Watson (*J. Indian Inst. Sci.*, 1932, **15**, *A*, 59) have determined two new equilibrium constants, at 503° and 403° K. Kennedy, Sagenkahn, and Aston (*J. Amer. Chem. Soc.*, 1941, **63**, 2267) found the entropy of methyl ether at 298·16° K. and 1 atm. to be 63·72 ± 0·20 E.U. in the ideal vapour state. This value for the ideal state may justifiably be combined with other data referring to an actual vapour, since the correction for gas imperfection is small (0·08 E.U.; *loc. cit.*), and the other thermochemical determinations are not of such high precision as this of entropy.

Kistiakowsky and Rice (*J. Chem. Physics*, 1940, **8**, 618) determined the molar heat capacity of methyl ether vapour at 272·2°, 300·76°, 333·25°, and 370·42° K.; these values when plotted against temperature give a straight line whose equation is:

$$\Delta C_p = 5{\cdot}40 + 0{\cdot}0335T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This equation gives the variation of heat capacity with temperature over the range 0—100°; strictly, any free-energy equation developed from it is valid only within this range, but extrapolation to higher temperatures should not involve much error.

Bischowsky and Rossini ("Thermochemistry of Chemical Substances," 1936) prefer a recalculated value for the heat of combustion of methyl ether based on Thomsen's value. From their values for the heats of combustion of methyl ether and methanol, and for the heat of vaporisation of water, we obtain: $2MeOH(v.) = Me_2O + H_2O$; $\Delta H^0_{291} = -7{,}300$ cals., and for the formation of methyl ether, $\Delta H^0_{291} = -46{,}400$ cals.

Using equation (1), we find:

$$2C + 3H_2 + 0{\cdot}5O_2 = C_2H_6O; \ \Delta H^0_{298\cdot1} = -46{,}500 \text{ cals.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The experimental equilibrium constants are: $K = 3{\cdot}18$ at 623° K. (McKee and Burke), 15·4 at 503° K., 48·5 at 403° K (both due to Gajendragad, Jatkar, and Watson). From these data, we can develop the free-energy equation

$$2MeOH\ (v.) = Me_2O + H_2O\ (v.); \ \Delta G^0 = -9100 - 10{\cdot}2T \log_e T + 0{\cdot}00142T^2 + 69{\cdot}58T \quad . \quad . \quad . \quad (3)$$

(The three values of the integration constant are −69·10, −69·14, and −70·5.) Hence

$$\Delta G^0_{298\cdot1} = -4{\cdot}420 \text{ cals.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Using Parks and Huffman's values for the free energies of the vapours of methanol and water, we obtain for the formation of methyl ether

$$2C + 3H_2 + 0{\cdot}5O_2 = C_2H_6O; \ \Delta G^0_{298\cdot1} = -27{,}700 \text{ cals.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The entropy of formation of methyl ether (from the value of Kennedy and co-workers, and atomic entropies) is

$$2C + 3H_2 + 0{\cdot}5O_2 = C_2H_6O; \ \Delta S^0_{298\cdot1} = -57{\cdot}3 \text{ E.U.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

From the third law, using $\Delta G = \Delta H - T.\Delta S$, we thus find:

$$2C + 3H_2 + 0{\cdot}5O_2 = C_2H_6O; \ \Delta G^0_{298\cdot1} = -29{,}400 \text{ cals.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

For the mean free-energy value, we may take

$$2C + 3H_2 + 0{\cdot}5O_2 = C_2H_6O; \ \Delta G^0_{298\cdot1} = -28{,}500 \text{ cals.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

This value is still somewhat uncertain, but it must be more reliable than that given by Parks and Huffman. The chief uncertainty lies in the heat of combustion of methyl ether. It may be noted that, if we assume $\Delta C_p = 0$ for the dehydration of methanol, we obtain $\log_e K = 7300/RT - 4{\cdot}8$, $\Delta G^0 = -7300 + 9{\cdot}6T$, and

$$2MeOH\ (v.) = Me_2O + H_2O\ (v.); \ \Delta G^0_{298\cdot1} = -4{,}440 \text{ cals.}$$

THE DYSON PERRINS LABORATORY, OXFORD. [*Received, September 17th*, 1943.]

---

# 156. 2 : 4-Diarylpyrroles. Part I. Synthesis of 2 : 4-Diarylpyrroles and 2 : 2′ : 4 : 4′-Tetra-arylazadipyrromethines.

By Maurice A. Thorold Rogers.

The intense blue colour formed when ketones of the type Ar·CH($CH_2$·$NO_2$)·$CH_2$·$COAr^1$ (I) or Ar·CH(CN)·$CH_2$·$COAr^1$ (II) or some of their simple derivatives and related compounds are heated with ammonium formate or with certain other nitrogen-containing compounds has been shown to be due to the formation of 2 : 2′ : 4 : 4′-tetra-arylazadipyrromethines (III), which constitute a new chromophoric system, having a formal relationship to the phthalocyanines. (III, Ar = $Ar^1$ = Ph) has been shown to have the structure assigned to it by degradation with hydriodic acid to 2 : 4-*diphenylpyrrole* (IV, Ar = $Ar^1$ = Ph), which is capable of reconversion into (III, Ar = $Ar^1$ = Ph) by nitrous acid, *via* 5-*nitroso*-2 : 4-*diphenylpyrrole* (V, Ar = $Ar^1$ = Ph), which condenses with a further molecule of (IV, Ar = $Ar^1$ = Ph).

(V, Ar = $Ar^1$ = Ph) has been reduced catalytically to give 5-*amino*-2 : 4-*diphenylpyrrole* (VII, Ar = $Ar^1$ = Ph), which differs from the known 3-amino-2 : 4-diphenylpyrrole (VIII).

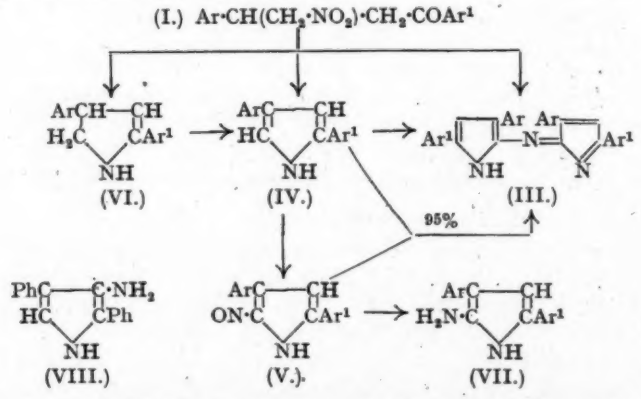
Certain metallic complexes of (III, Ar = $Ar^1$ = Ph) and a few analogues of types (III) and (IV) are described.

In the course of experiments made with the object of synthesising the compound

Ph·CH($CH_2$·$NO_2$)·$CH_2$·CHPh·$NH_2$,

the action of ammonium formate and formamide on the nitrobutyrophenone Ph·CH($CH_2$·$NO_2$)·$CH_2$·COPh (I, Ar = $Ar^1$ = Ph) (Kohler, *J. Amer. Chem. Soc.*, 1916, **38**, 889) was tried, the conditions of the Leuckart reaction (Ingersoll, Brown, Kim, Beauchamp, and Jennings, *ibid.*, 1936, **58**, 1808) being used. In place of the expected formyl derivative of the amine there was formed an intensely blue compound. The nitrobutanone was heated with 3—5 times its weight of formamide (under reflux) or ammonium formate (under distillation conditions) to 180—200°, at which temperature it was maintained for a further ½ hour. The first sign of colour appeared at about 120°, the oily droplets of the nitrobutanone acquiring a blue tint; this rapidly increased in intensity, and after 5—10 minutes' boiling the surface of the liquid acquired a coppery sheen, due to the separation of the blue material in crystalline form. After cooling, the melt was extracted with alcohol, leaving a dark microcrystalline powder, which was purified by crystallisation from nitrobenzene or β-ethoxyethyl alcohol. Analysis suggested the formula $C_{32}H_{23}N_3$. Molecular weight determinations eliminated the possibility of a molecule of double this weight.

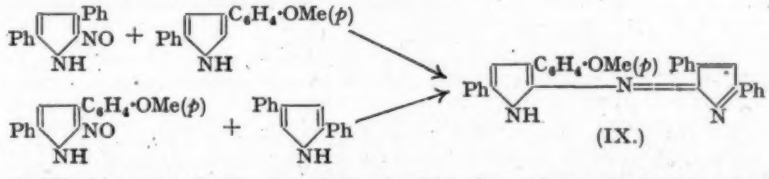
Interest in the new blue compound was enhanced by two observations: (1) its stability was such that it could be sublimed with little decomposition merely by heating at atmospheric pressure, giving violet vapours which condensed on a cool surface to yield the original blue compound; (2) a solution of the blue compound in moist dioxan, pyridine or β-ethoxyethyl alcohol was reduced by alkaline sodium hydrosulphite to a nearly colourless leuco-compound, which was readily reoxidised by air to the original material. The high melting point (287—288°) and intense colour of the material and its tendency to sublime near the melting point made mixed melting points unreliable, and identity of samples was established by the reproducibility of the two phenomena just referred to; by the formation of characteristic short needles when a β-ethoxyethyl-alcoholic solution was allowed to evaporate on a microscope slide; by the appearance of the solution in, for example, nitrobenzene, which was deep blue to reflected, but intense crimson to transmitted light; and finally by the bleaching of the colour when a solution in pyridine was boiled for ¼—½ hour with hydroxylamine hydrochloride (a reaction which will be discussed in a later paper).




Experiments conducted to establish the structure of this compound, consisting of variations of one or other of the constituents of the melt process, eliminated some possibilities, but failed to show the actual structure, which was proved to be 2 : 2′ : 4 : 4′-*tetraphenylazadipyrromethine* (III, Ar = $Ar^1$ = Ph) by the following steps: on boiling with 55% hydriodic acid, the blue compound was decomposed to a colourless compound, $C_{16}H_{13}N$, which was also isolated in small yield as a by-product in the ammonium formate reaction. That this compound was 2 : 4-*diphenylpyrrole* (IV, Ar = $Ar^1$ = Ph) was shown by its preparation from the

pyrroline (VI, Ar = Ar¹ = Ph) (Sonn, *Ber.*, **1935**, **68**, 148; Rupe and Gisiger, *Helv. Chim. Acta*, **1925**, **8**, 338) by selenium dehydrogenation. Nitrosation of pyrroles usually occurs in the β-position (cf. Fischer and Orth, "Die Chemie des Pyrroles," vol. I, p. 104), but 2 : 4-diphenylpyrrole was nitrosated readily by the action of nitrous acid in the α-position, for reduction (catalytic) of the nitroso-compound (V, Ar = Ar¹ = Ph) gave an aminopyrrole (VII, Ar = Ar¹ = Ph) which differed from the known 3-amino-2 : 4-diphenylpyrrole (VIII) (Gabriel, *Ber.*, 1908, **41**, 1138; Gabriel did not consider the constitution of his 3-amino-compound as proved, but the investigations described in Part III leave no doubt that his formula is correct), and was therefore considered to be the 5-*amino*-compound. This 5-*nitroso*-2 : 4-*diphenylpyrrole* (V, Ar = Ar¹ = Ph) condensed readily with a further molecule of 2 : 4-diphenylpyrrole (IV, Ar = Ar¹ = Ph) to give high yields of the blue compound (III, Ar = Ar¹ = Ph).

There remains only the remote possibility that the compound is asymmetric, the α-nitroso-compound condensing with the β-position of the second molecule of the diarylpyrrole. That this was not the case was shown by preparing the methine (IX) by the two routes shown; the identity of the two preparations was established by examination of the *X*-ray diffraction patterns.




(IX.)

The formation of (III) from the nitrobutyrophenones (I) or from the cyano-ketones Ar·CH(CN)·$CH_2$·COAr¹ (II) constitutes a remarkable reaction, the mechanism of which will be discussed in a later communication. The reaction is not appreciably affected by substituents in either of the aryl nuclei; the azamethines listed in Table I have been prepared.

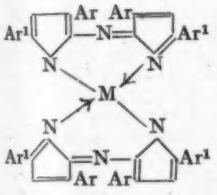
TABLE I.

*Reaction of ammonium formate on compounds* (I) *and* (II).

| (I). | | (II). | | Azamethine (III). | |
|---|---|---|---|---|---|
| Ar. | Ar.¹ | Ar. | Ar¹. | M. p. | Reflex colour of crystals. |
| $C_6H_4$·$NO_2$(*m*) | Ph | — | — | 330° | Bright green |
| $C_6H_4$·OH(*m*) | Ph | — | — | 304—306 | Violet |
| $C_6H_4$·$NMe_2$(*p*) | Ph | — | — | 276—278 | Copper |
| $C_6H_3$:$O_2CH_2$(3 : 4) | — | — | — | 258—259 | Copper-brown |
| Ph | C6H4·OMe(p) | Ph | C6H4·OMe(p) | 239—242 | Dull blue |
| C6H4·OMe(p) | Ph | C6H4·OMe(p) | Ph | 288—290 | Bright green |
| C6H4·OMe(p) | C6H4·OMe(p) | | | 281—282 | Bluish-copper |
| | | C6H4·NHAc(p) | Ph | (*ca.*) 370° | Dull violet |

These azamethines are very similar in colour in solution, but the reflex colour of the crystals varies over a wide range. Where the substituent is salt-forming, the azamethine shows some water solubility at the appropriate pH, and the dimethylamino-substituted azamethine gives a water-soluble quaternary salt with methyl iodide. The majority of the substituted azamethines have lower solubility than the parent compound.

The reaction calls to mind the "urea melt" process of B.P. 464,126, in which metal phthalocyanines are made by heating phthalic anhydride and a metal salt with urea [urea does actually give some azamethine when fused with (I)]. Indeed, the azamethine bears a certain formal relationship to phthalocyanine, which is an azaporphyrin. The resemblance to phthalocyanines is further pointed by the formation from the azadipyrromethines of metallic complexes, which give analytical figures agreeing well with structure (X). *Zinc*, *copper*, *nickel* and *cobalt* complexes have been made, and it is noteworthy that, whereas the compound (III) is not fast to light when rubbed out as a print, the copper complex (X, M = Cu) has an excellent light fastness, being equal to Prussian-blue in this respect. A similar disparity is shown between metal-free phthalocyanine and its copper complex.




(X.)

No earlier examples of the azadipyrromethine series appear to have been made and the system constitutes a new chromophore. The ease of formation and stability seem largely to be accounted for by the reactivity conferred on the α-position by the two suitably placed phenyl groups. There does not seem to be any corresponding increase in reactivity of the β-position, and it is noteworthy that, whereas 3-amino-2 : 4-diphenylpyrrole (Gabriel, *loc. cit.*) is a stable compound, the corresponding 5-amino-compound (VII, Ar = Ar¹ = Ph) is very reactive, and is readily oxidised by air, tetraphenylazadipyrromethine being among the products.

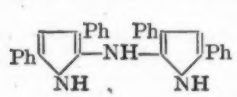
The isolation of the two "halves" of the azamethine makes available two new reactive systems capable of reacting with a wide variety of substances: 5-nitroso-2 : 4-diphenylpyrrole (V, Ar = Ar¹ = Ph) with compounds which contain a reactive methylene group and 2 : 4-diphenylpyrrole itself with compounds which normally react with reactive methylene groups. Examples of such condensations, which occur in acetic acid–acetic anhydride, are given in the following paper.

Attention has been directed to the preparation of 2 : 4-diphenylpyrrole in good yield; β-benzoyl-α-phenylpropionitrile, which can be made in yields of 96% by the method of Allen and Kimball (*Org. Synth.*, Vol. X, 80), can be reduced to 2 : 4-diphenylpyrroline catalytically with Raney nickel in yields exceeding 95% (compare Rupe and Gisiger, *Helv. Chim. Acta*, 1925, **8**, 338). The selenium dehydrogenation of 2 : 4-diphenylpyrroline, already referred to, presents some unusual features; only traces of hydrogen selenide are evolved and the bulk of the selenium can be recovered unchanged at the end of the reaction, which is quite rapid at 250°. No other examples of selenium-catalysed dehydrogenations have been traced. Yields higher than 55% could not be obtained, owing to the formation of by-products, among them a hydrocarbon, which is probably $CHPhMe{\cdot}CH_2{\cdot}CH_2Ph$. The mechanism of the formation of this compound is obscure, but the missing nitrogen atom can be detected as ammonia in the issuing gases. Dehydrogenation can also be effected with Raney nickel in the liquid phase (350°); again the yield is 55%, and ammonia is evolved. A more satisfactory process for the dehydrogenation of the pyrroline has been worked out by my colleague Dr. P. V. Youle, who obtained yields exceeding 80% by passing the pyrroline over a nickel catalyst on a pumice substrate at 350°.

Syntheses of 2 : 4-diarylpyrroles with substituents in the aryl nuclei proceed satisfactorily by this series of reactions, and 2-*phenyl*-4-p-*anisylpyrrole* (IV; $Ar^1$ = Ph, Ar = $C_6H_4{\cdot}OMe$) and 4-*phenyl*-2-p-*anisylpyrrole* (IV; Ar = Ph, $Ar^1$ = $C_6H_4{\cdot}OMe$) have thus been made.

2 : 4-Diphenylpyrrole is a very weak base, but its 5-nitroso-derivative is a relatively strong base, forming salts with strong acids. The free base is a typical green nitroso-compound, which causes dermatitis in some subjects.

Tetraphenylazadipyrromethine is slightly basic; it forms a perchlorate which can be isolated, but dissociates rapidly in solution. The nature of the unstable reduction products obtained by treating the azamethine with various reducing agents is obscure. When the pigment, *e.g.*, in aqueous dioxan, is treated with an alkaline solution of glucose, a red reduction product is obtained, which is readily reoxidised in air. This red " leuco "-compound is further reduced by sodium hydrosulphite to a substance with a pale yellowish-pink colour, which is also obtained direct from the azamethine by hydrosulphite. The oxidation, even when the reduction has been carried out by hydrosulphite alone, can frequently be observed to pass through a red stage. Dilution with water at the colourless stage precipitates a white solid, which rapidly becomes blue when exposed to the air. The view is held that the glucose reduction product is the true leuco-compound (annexed formula) and the hydrosulphite reduction product is an addition complex with the reducing agent. The metallic complexes can also be reduced to colourless leuco-compounds, but the metal atom is removed by the process.




This work is the subject of pending patent applications.

## Experimental.

Analyses by Mr. E. S. Morton. M. p.'s are uncorrected.

A. *Tetra-arylazadipyrromethines by the Ammonium Formate Melt Process.*—2 : 2′ : 4 : 4′-*Tetraphenylazadipyrromethine* (III, Ar = $Ar^1$ = Ph). γ-Nitro-β-phenylbutyrophenone (Kohler, *loc. cit.*) (150 g.) and ammonium formate (430 g.) were heated during ½ hr. to 180°, and then at 190° for a further ½ hr. Ammonia was evolved, followed, suddenly, at 180°, by formic acid (condensate decolourised potassium permanganate) and a little solid, probably diphenylpyrrole, steam-distilled out of the flask. After cooling to 70°, the mixture was triturated with methyl alcohol, the liquid filtered, and the residue washed thoroughly with methyl alcohol, the total filtrates being worked up as described below, and dried at 100° (54 g.). Recrystallisation from nitrobenzene gave short, dark copper-coloured needles (32 g., with a further 8·7 g. from the filtrate by concentration). The uncrystallised material probably contained other strongly coloured compounds, not isolated by any method tried (including chromatographic analysis).

The *azamethine* was very sparingly soluble in water, methyl or ethyl alcohol (very pale blue-violet colour), and petrol; addition of a drop of a strong acid to an alcoholic suspension produced a deep greenish-blue solution, from which the azamethine was reprecipitated by alkali. It was slightly soluble in hot butanol, benzene or acetone, more soluble in hot nitrobenzene, β-ethoxyethyl alcohol, xylene, pyridine, dioxan, formodimethylamide or camphor. It was also readily soluble in cold concentrated sulphuric acid, being reprecipitated unchanged if the solution was diluted immediately, but if it was kept for 2—3 hours and then poured on ice, a clear olive-green solution was obtained, which on boiling deposited a brilliant green powder; this contained sulphur, was soluble in dilute alkali and ammonia, to a pale olive-green solution, and was reprecipitated by acids. The azamethine sublimed without decomposition at 5 mm. and with slight decomposition at atmospheric pressure; the vapours were violet. M. p. 287—288° [Found: C, 85·65; H, 4·9; N, 9·35; *M* (Menzies–Wright differential method, using benzene), 430, 460. $C_{32}H_{23}N_3$ requires C, 85·5; H, 5·1; N, 9·4%; *M*, 449].

2 : 4-*Diphenylpyrrole from the ammonium formate reaction.* The permanganate-coloured methanol extract from the previous experiment was poured into water and the solid was collected, dried, and dissolved in benzene (charcoal). The filtered solution was concentrated until, on cooling, solid crystallised; this was collected, and the concentration and crystallisation of the filtrate repeated. The combined solids were dissolved in ethyl alcohol (charcoal), filtered, and fractionally precipitated by the addition of water. The first fraction was blue (m. p. 172°) and was discarded. The main fraction, after drying, crystallised from benzene in long, white, flattened needles (0·62 g.), m. p. 178—179°, identical with 2 : 4-diphenylpyrrole prepared synthetically.

2 : 2′-*Diphenyl*-4 : 4′-*di*-(m-*nitrophenyl*)*azadipyrromethine* (III; Ar = $C_6H_4{\cdot}NO_2$, $Ar^1$ = Ph). 3-Nitrochalkone (Sorge, *Ber.*, 1902, **35**, 1068) (25·3 g.) was dissolved in hot methyl alcohol (200 c.c.), cooled to 35°, nitromethane (9·1 g.) added, a solution of sodium (3·45 g.) in methyl alcohol (100 c.c.) run in and the mixture warmed on the steam-bath under reflux for 10 minutes. The cooled solution (0°) was acidified with acetic acid (20 c.c.); the precipitated oil rapidly solidified. Crystallised from methyl alcohol, γ-*nitro*-β-(m-*nitrophenyl*)*butyrophenone* formed needles, m. p. 74—77° (Found: N, 9·05. $C_{16}H_{14}O_5N_2$ requires N, 8·95%). This nitro-ketone (10 g.) was heated with ammonium formate (30 g.) to 180° during ½ hr. The cooled melt was extracted with alcohol, and the residual greenish solid crystallised

from nitrobenzene; the *azamethine* formed needles with a bright green reflex (2·8 g.), m. p. 330° (Found: C, 71·15; H, 4·05; N, 13·05. $C_{32}H_{21}O_4N_5$ requires C, 71·25; H, 3·9; N, 13·0%). It was less soluble than the parent azamethine. It was reduced by sodium hydrosulphite in aqueous dioxan to a pink leuco-compound.

2 : 2′-*Diphenyl*-4 : 4′-*di*-(m-*hydroxyphenyl*)*azadipyrromethine* (III; Ar = $C_6H_4$·OH, $Ar^1$ = Ph). 3-Hydroxychalkone (Bablich and Kostanecki, *Ber.*, 1896, **29**, 235) (22·4 g.) in methyl alcohol (100 c.c.), nitromethane (9·1 g.), and a solution of sodium (6·9 g.) in methyl alcohol (20 c.c.), added during 1 hour, gave a deep yellow solution. Ice (200 g.) was added and the solution was cooled to − 5° and acidified with acetic acid (20 c.c.). Addition of water precipitated an oil, which was extracted in ether, dried (calcium chloride), and recovered. It slowly solidified, forming hard prisms, but some oily material remained. A sample was pressed on a porous tile and recrystallised from benzene, from which *γ-nitro-β-*(m-*hydroxyphenyl*)*butyrophenone* separated very slowly in pale yellow-brown prisms, m. p. 96—98° (Found: C, 67·7; H, 5·0; N, 4·95. $C_{16}H_{15}O_4N$ requires C, 67·35; H, 5·25; N, 4·9%). The crude oily nitrobutyrophenone was heated to 160° with ammonium formate (5 parts). Colour formation was very rapid. The residual *azamethine* after alcohol extraction crystallised from nitrobenzene in short needles with a violet reflex, m. p. 304—306° (Found: C, 79·6; H, 4·8; N, 8·85. $C_{32}H_{22}O_2N_2$ requires C, 79·8; H, 4·8; N, 8·7%). A paste with dioxan, treated with a little 2N-sodium hydroxide and diluted with water, gave a deep blue aqueous solution, which was reduced reversibly to a colourless solution with sodium hydrosulphite.

2 : 2′-*Diphenyl*-4 : 4′-*di*-(p-*dimethylaminophenyl*)*azadipyrromethine* (III; Ar = $C_6H_4$·$NMe_2$, $Ar^1$ = Ph). Into 4-dimethylaminochalkone (MacLean and Widdows, J., 1914, **105**, 2173) (10 g.), methyl alcohol (100 c.c.), and nitromethane (3·6 g.), heated to solution and cooled to 25°, was run a solution of sodium (1·4 g.) in methyl alcohol (50 c.c.); the mixture was refluxed for 1 hour on the steam-bath, cooled to 5°, and acidified with acetic acid (5 c.c.). The yellow oil obtained rapidly solidified and after crystallisation from alcohol *γ-nitro-β-*(p-*dimethylaminophenyl*)*butyrophenone* (8·5 g.) separated in pale yellow needles, m. p. 114—115° (Found: N, 9·25. $C_{18}H_{20}O_3N_2$ requires N, 9·0%). The *oxime* crystallised from alcohol in colourless needles, m. p. 121—123° with formation of a yellow liquid (Found: N, 13·05. $C_{18}H_{21}O_3N_3$ requires N, 12·85%). The nitrobutyrophenone, on heating with ammonium formate (5 parts), gave the *azamethine*, which separated from *β*-ethoxyethyl alcohol in flat needles with curved edges, with a bright coppery reflex, m. p. 276—278° (Found: C, 80·8; H, 6·05; N, 12·7. $C_{36}H_{35}N_5$ requires C, 80·45; H, 6·5; N, 13·0%). It was slightly soluble in dilute acids. On standing with methyl iodide in nitrobenzene solution for 24 hours, it formed a *dimethiodide*, which was soluble in water and in alcohol to form deep blue solutions, and insoluble in acetone (Found for the ether-washed product: N, 8·75; I, 29·25. $C_{38}H_{39}N_5I_2$ requires N, 8·55; I, 31·0%). The quaternary salt is a wool dye.

2 : 2′-*Diphenyl*-4 : 4′-*di*-(3 : 4-*methylenedioxyphenyl*)*azadipyrromethine* (III; Ar = $C_6H_3{:}O_2CH_2$, $Ar^1$ = Ph). γ-Nitro-*β*-(3 : 4-methylenedioxyphenyl)butyrophenone (50 g.), obtained as an oil (Kohler and Drake, *J. Amer. Chem. Soc.*, 1923, **45**, 2144, give m. p. 95—96°), was heated with ammonium formate (75 g.) as previously described. After extraction of the melt with alcohol and crystallisation of the residue from *β*-ethoxyethyl alcohol, the *azamethine* was obtained in copper-brown needles, m. p. 258—259° (Found: C, 75·9; H, 4·25; N, 7·9. $C_{34}H_{23}O_4N_3$ requires C, 76·0; H, 4·3; N, 7·8%).

2 : 2′-*Di*-p-*anisyl*-4 : 4′-*diphenylazadipyrromethine* (III; Ar = Ph, $Ar^1$ = $C_6H_5$·OMe). Into benzylidene-*p*-methoxyacetophenone (Stockhauser and Gattermann, *Ber.*, 1892, **25**, 3538) (23·8 g.) and nitromethane (9·2 g.) in methyl alcohol (100 c.c.) was run sodium (3·0 g.) in methyl alcohol (100 c.c.); the mixture was warmed at 50° for ½ hour, cooled, and acidified with acetic acid, and water added. *γ-Nitro-β-phenyl-*p-*methoxybutyrophenone* separated slowly in prisms or thick plates, m. p. 92—93° after recrystallisation from alcohol (Found: C, 68·15; H, 5·7; N, 4·65. $C_{17}H_{17}O_4N$ requires Cl, 68·2; H, 5·7; N, 4·7%). The *azamethine*, prepared from it by heating with ammonium formate, formed dull blue, broad flat needles or plates with a tendency to show curved edges, m. p. 239—242° (Found: C, 79·65; H, 5·05; N, 8·3. $C_{34}H_{27}O_2N_3$ requires C, 80·1; H, 5·3; N, 8·2%).

2 : 2′-*Diphenyl*-4 : 4′-*di*-p-*anisylazadipyrromethine* (III; Ar = $C_6H_4$·OMe, $Ar^1$ = Ph). 4-Methoxychalkone was converted into *γ-nitro-β-*p-*anisylbutyrophenone* by the method described for the isomeric compound (above). It was crystallised with difficulty from alcohol and then from benzene; m. p. 66° after previous sintering (Found: C, 67·45; H, 5·45; N, 4·5. $C_{17}H_{17}O_4N$ requires C, 68·2; H, 5·7; N, 4·7%). The *azamethine* crystallised from nitrobenzene in large needles with a bright greenish metallic reflex, m. p. 288—290° (Found: C, 79·7; H, 5·7; N, 8·55. $C_{34}H_{27}O_2N_3$ requires C, 80·15; H, 5·3; N, 8·25%). From the alcoholic filtrates of the ammonium formate melt process a little 2-phenyl-4-*p*-anisylpyrrole was obtained, which crystallised from benzene in silvery plates, m. p. 198—200°, identical with a synthetic specimen.

2 : 2′ : 4 : 4′-*Tetra*-p-*anisylazadipyrromethine* (III, Ar = $Ar^1$ = $C_6H_4$·OMe). To anisylidene-*p*-methoxyacetophenone (Stauss, *Annalen*, 1910, **374**, 139) (52 g.) and nitromethane (18·5 g.) in methyl alcohol (500 c.c.) was added sodium (7·1 g.) in methyl alcohol (220 c.c.). When reaction was complete, and the temperature began to fall, the mixture was cooled below 0° and acidified with acetic acid. The oil obtained on addition of water was extracted with ether and dried over calcium chloride, and the ether distilled; *γ*-nitro-*β*-anisyl-*p*-methoxybutyrophenone was left as an oil. The *azamethine* made from it crystallised from pyridine in flat bluish-coppery needles, m. p. 281—282° (Found: C, 76·2; H, 5·6. $C_{36}H_{31}O_4N_3$ requires C, 75·95; H, 5·5%).

2 : 2′-*Diphenyl*-4 : 4′-*di*-(p-*acetamidophenyl*)*azadipyrromethine* (III; Ar = $C_6H_4$·NHAc, $Ar^1$ = Ph). *p*-Acetamidochalkone was made by condensing *p*-acetamidobenzaldehyde and acetophenone in alcohol with sodium hydroxide as catalyst. It had m. p. 180—182° (cf. Kauffman and Burckhardt, *Ber.*, 1913, **46**, 3811). The chalkone (34·4 g.) in methyl alcohol (500 c.c.) and powdered sodium cyanide (25·5 g.) were heated under reflux, and a mixture of acetic acid (24 c.c.) and water (65 c.c.) run in during 20 mins. After a further 20 mins.' boiling, the solution was cooled and poured into ice and water, and the white solid collected and washed until the filtrate was free from cyanide; *β-benzoyl-α-*(p-*acetamidophenyl*)*propionitrile* formed very pale yellow prisms or needles (12·2 g.), m. p. 163—164·5°, from ethanol (Found: C, 73·9; H, 5·4; N, 9·6. $C_{18}H_{16}O_2N_2$ requires C, 74·0; H, 5·5; N, 9·6%). When heated with ammonium formate for 10 minutes at 190°, the nitrile gave the *azamethine*, which formed dull violet needles, m. p. *ca.* 370°, from nitrobenzene (Found: C, 76·6; H, 5·05; N, 12·6. $C_{36}H_{29}O_2N_5$ requires C, 76·7; H, 5·15; N, 12·4%).

B. *Metallic Complexes of the Azamethines.—Copper bis-*(2 : 2′ : 4 : 4′-*tetraphenylazadipyrromethine*) (X) was obtained by refluxing the azamethine (1·0 g.) and copper acetate (0·5 g.) in butyl alcohol (50 c.c.) for ½ hour. The coppery-brown precipitate (1·0 g.), which appeared as minute, diamond-shaped prisms under the microscope, crystallised from formodimethylamide in well-formed prisms (Found: C, 80·1; H, 4·4; N, 8·75; Cu, 6·5. $C_{64}H_{44}N_6Cu$ requires C, 80·05; H, 4·6; N, 8·75; Cu, 6·6%). The complex was somewhat soluble in nitrobenzene, dioxan and pyridine, but less soluble than the azamethine in butyl alcohol and *β*-ethoxyethyl alcohol. The solutions were blue to transmitted light, in contrast to the crimson colour of solutions of the azamethine. *Cobalt bis-*(2 : 2′ : 4 : 4′-*tetraphenylazadipyrromethine*), from the azamethine and cobalt acetate in butyl alcohol, was not readily crystallised; it was dissolved in nitrobenzene, and the filtered solution concentrated to small volume. The complex formed small hexagonal prisms (Found: C, 78·95; H, 4·55; N, 9·1; Co, 5·9. $C_{64}H_{44}N_6Co$ requires C, 80·4; H, 4·6; N, 8·8; Co, 6·2%). The *nickel* (Found: C, 80·95; H, 4·6; N, 9·15; Ni, 6·3. $C_{64}H_{44}N_6Ni$ requires C, 80·4; H, 4·6; N, 8·8; Ni, 6·2%) and the *zinc*

complex (Found: C, 80·0; H, 4·75; N, 8·65; Zn, 7·1. $C_{44}H_{44}N_6Zn$ requires C, 79·9; H, 4·6; N, 8·7; Zn, 6·8%) were prepared.

C. 2 : 4-*Diarylpyrroles.*—2 : 4-*Diphenylpyrrole* (IV, Ar = Ar¹ = Ph). β-Benzoyl-α-phenylpropionitrile (120 g.), suspended in methyl alcohol or ethyl acetate (800 c.c.), and Raney nickel (about 20 g.) were shaken rapidly in a hydrogenator at atmospheric temperature and pressure. If less catalyst was used, reduction was very slow; if more, reduction tended to continue, with no very noticeable break in the curve, to the pyrrolidine, recognised as its phenylthiourea (Rupe and Gisiger, *loc. cit.*). When the theoretical amount of hydrogen had been absorbed (23 l.), the solution was filtered, and the solvent distilled. The residue was distilled in a vacuum, giving 2 : 4-diphenylpyrroline, m. p. about 40°; yield, 105 g. (95%). Rupe and Gisiger obtained 15—16 g. from 30 g. of the nitrile.

*Dehydrogenation.* (a) Traces of the pyrrole were obtained on prolonged heating of the pyrroline at 350°. (b) The pyrroline (5·0 g.) was heated with selenium (5·0 g.) in a Kjeldahl flask fitted with an inlet tube reaching to just above the surface of the contents, through which a very slow stream of nitrogen or carbon dioxide was passed. The flask was heated at 250° for 3 hours and the issuing vapours were passed into lead nitrate solution. On cooling, the pyrrole solidified on the button of selenium as a light grey solid, and was extracted with hot toluene. The residual selenium weighed 4·5 g., and from the lead selenide solution 0·43 g. of lead selenide was obtained. From the toluene extract 2·7 g. (55%) of 2 : 4-diphenylpyrrole were obtained. When the experiment was conducted on a larger scale (the lead nitrate solution was dispensed with when the experiment was conducted for purely preparative purposes) there was obtained from the toluene mother-liquors by repeated concentration and crystallisation a small oily residue, which was distilled in a vacuum, b. p. 175°/17 mm., 228°/760 mm., giving a colourless oil with a pleasant smell. This b. p. accords reasonably well with that given by Stobbe and Posnjak (*Annalen*, 1909, **371**, 297) for αγ-diphenylbutane and analysis also suggests this structure (Found: C, 91·05; H, 8·2; N, 0·5. Calc. for $C_{16}H_{18}$: C, 91·4; H, 8·6%). (c) *By Raney nickel* (liquid phase). This was carried out as in (b) except that the temperature was maintained at 350°. Yields were of the order of 50%, and the toluene portion had the same sweet smell as had the αγ-diphenylbutane isolated from the selenium dehydrogenation. (d) *Vapour phase dehydrogenation* (P. V. Youle). Various catalysts were tried, each held in a Pyrex tube (3 cm. in diameter, 30 cm. long) heated in an electric furnace. The best results were obtained from a nickel-on-pumice catalyst, made by igniting pumice fragments (16—32 mesh) impregnated with nickel nitrate. Before use the catalyst was reduced with hydrogen at 400—450°. At 350°, diphenylpyrroline was passed over the reduced catalyst (2 mols./hr./l. catalyst, the pyrroline being either molten or dissolved in its own weight of benzene). During and after the addition a rapid flow of carbon dioxide was used to blow out the product. Yield of pure diphenylpyrrole, m. p. 176—178° after one recrystallisation from toluene, 83%. 2 : 4-Diphenylpyrrolidine was dehydrogenated as readily as the pyrroline in all the dehydrogenation processes.

2 : 4-*Diphenylpyrrole* crystallised from toluene or ligroin (b. p. 100—120°) in long, white, flattened needles, m. p. 180° (Found: C, 86·5, 86·5, 87·2; H, 5·75, 5·75, 5·7; N, 6·45, 6·7, 6·45. $C_{16}H_{13}N$ requires C, 87·7; H, 5·9; N, 6·4%. The low value for carbon is remarkable, especially as the solvent in each case was a hydrocarbon). It was soluble in most hot organic solvents; the solution in acetic acid became blue on heating. It dissolved in concentrated sulphuric acid to give a canary-yellow solution; the colour faded on heating, became strongly violet on stronger heating, and then disappeared on dilution. The diphenylpyrrole gave a blue colour with Ehrlich's reagent. It coupled (in alcoholic solution, acidified with hydrochloric acid) with diazo-compounds (with diazotised-2 : 5-dichloroaniline, dull brick-red; with diazotised-*p*-nitroaniline, reddish-violet; with diazotised-5-chloro-*o*-toluidine, wine-red). A very sensitive test for 2 : 4-diarylpyrroles is the rapid formation of the blue azamethine when the diarylpyrrole is treated in the cold with a solution of 5-nitroso-2 : 4-diphenylpyrrole hydrochloride in acetic anhydride. 2 : 4-Diphenylpyrrole formed a picrate and a platinichloride, but both dissociated on attempted recrystallisation.

4-*Phenyl*-2-p-*anisylpyrrole* (IV; Ar¹ = $C_6H_4$·OMe, Ar = Ph). β-*p*-Anisoyl-α-phenylpropionitrile (Kohler and Leers, *J. Amer. Chem. Soc.*, 1934, **56**, 981) was reduced with Raney nickel as described for the unsubstituted compound. 4-*Phenyl*-2-p-*anisylpyrroline* b. p. 235—250°/7 mm., crystallised from ether in large, pale yellow, waxy prisms, m. p. 74—75° (Found: C, 81·15; H, 6·45; N, 5·75. $C_{17}H_{17}ON$ requires C, 81·3; H, 6·8; N, 5·6%). It gave a picrate, long canary-yellow needles from alcohol, m. p. 180—181° (Found: N, 12·05. $C_{17}H_{17}ON,C_6H_3O_7N_3$ requires N, 11·7%). The pyrroline was dehydrogenated by selenium as described for the unsubstituted compounds; the *pyrrole* crystallised from benzene or toluene in white plates or thin broad needles, m. p. 205—207° (Found: C, 81·6; H, 5·95; N, 5·8. $C_{17}H_{15}ON$ requires C, 81·9; H, 6·05; N, 5·65%). It dissolved in concentrated sulphuric acid to a yellow solution, the colour of which faded on warming, then darkened, and finally became olive-green.

2-*Phenyl*-4-p-*anisylpyrrole* (IV; Ar¹ = Ph, Ar = $C_6H_4$·OMe.) β-Benzoyl-α-*p*-anisylpropionitrile was made by the method of *Organic Syntheses* (Coll. Vol. I, 71), the appropriate amount of anisaldehyde being used in place of benzaldehyde; yield 76·5%, m. p. 114—116° (Robertson and Stephens, J., 1931, 963, give m. p. 118°). Catalytic reduction with Raney nickel gave 2-*phenyl*-4-p-*anisylpyrroline*, b. p. 232—238°/7 mm., s. p. 27° (Found: N, 6·05. $C_{17}H_{17}ON$ requires N, 5·6%). The pyrroline was probably contaminated with a little of the pyrrolidine, as hydrogen absorption continued beyond the theoretical end-point (cf. Rupe and Gisiger, *loc. cit.*). The pyrroline gave a *picrate*, pale yellow leaflets from alcohol, m. p. 156—158° (Found: N, 11·7. $C_{17}H_{17}ON,C_6H_3O_7N_3$ requires N, 11·7%). Dehydrogenation was effected with selenium at 250°, whereby the *pyrrole* was obtained in leaflets, m. p. 197—199°, identical with the material isolated as a by-product in the corresponding ammonium formate melt process (Found: C, 81·55; H, 5·75; N, 5·9. $C_{17}H_{15}ON$ requires C, 81·9; H, 6·05; N, 5·6%). It was soluble in cold concentrated sulphuric acid to give a yellow solution, which became progressively green and then violet-blue on warming.

D. *Nitrosation of* 2 : 4-*Diarylpyrroles.*—(1) A solution of 2 : 4-diphenylpyrrole (5·0 g.) in hot alcohol (250 c.c.) was cooled and to the suspension concentrated hydrochloric acid was added, followed by sodium nitrite (1·8 g.) in water (20 c.c.) during 10 minutes. The deep red-brown solution was filtered, and concentrated hydrochloric acid (25 c.c.) added, whereupon 5-*nitroso*-2 : 4-*diphenylpyrrole hydrochloride* crystallised in long, hair-like, brown needles. These were washed with acetone [yield, 5·8 g.; m. p. 190° (decomp.) with formation of the azamethine] and purified for analysis by dissolution in the minimum quantity of warm alcohol and dilution of the filtered solution with acetone, the hydrochloride separating in orange-brown needles (Found: C, 67·2; H, 4·45; N, 9·4. $C_{16}H_{12}ON_2,HCl$ requires C, 67·1; H, 4·55; N, 9·85%). The *base* (V, Ar = Ar¹ = Ph) was obtained from the hydrochloride in alcoholic solution by addition of alcoholic sodium acetate until the colour changed to yellow. The mixture was poured into cold water containing a little caustic soda or ammonia, and kept until the base had separated as a green solid; this was collected, washed with water, dried in a vacuum, and crystallised from alcohol, benzene or ether–petrol, forming green needles, m. p. 139—140° (Found: C, 77·2; H, 4·8; N, 11·05. $C_{16}H_{12}ON_2$ requires C, 77·4; H, 4·85; N, 11·3%). The *picrate* formed scarlet needles from benzene, m. p. 188° (decomp.) (Found: N, 14·6. $C_{16}H_{12}ON_2,C_6H_3O_7N_3$ requires N, 14·7%).

Nitrosation of diphenylpyrrole was also carried out by dissolving it (5·0 g.) in sulphuric acid (20 c.c.), running the yellow solution slowly into stirred ice and water, and treating the mixture with 5% sodium nitrite solution until a permanent positive nitrous acid test showed to starch–iodide paper (excess of nitrous acid does not seem to have any deleterious effect on the product). The crystalline paste was collected, and the orange sulphate dissolved in alcohol and converted into the green nitroso-base as described above. Yield, 5·0 g.

(2) A solution of 2-phenyl-4-*p*-anisylpyrrole (6·0 g.) in hot acetic acid (100 c.c.) was cooled, concentrated hydrochloric acid (5·0 c.c.) added, and nitrosation carried out with sodium nitrite (1·8 g.) in water. From the deep permanganate-purple solution, *5-nitroso-2-phenyl-4-anisylpyrrole hydrochloride* separated on addition of concentrated hydrochloric acid (10 c.c.). It was collected, washed with a mixture of acetic acid (5 c.c.) and concentrated hydrochloric acid (1 c.c.), and crystallised from alcohol by cautious addition of ether, separating in small diamond-shaped prisms, red to transmitted light, or elongated prisms or needles (Found : N, 8·75. $C_{17}H_{14}O_2N_2$,HCl requires N, 8·9%). The free *base* (V; $Ar^1$ = Ph, Ar = $C_6H_4$·OMe) was obtained from the hydrochloride as described for the unsubstituted compound; a yellow precipitate, which rapidly became green, was formed on pouring into water. From alcohol it formed green needles, m. p. 176—177° (decomp.) (Found : N, 10·0. $C_{17}H_{14}O_2N_2$ requires N, 10·1%).

(3) 4-Phenyl-2-*p*-anisylpyrrole was nitrosated as was the unsubstituted pyrrole. *5-Nitroso-4-phenyl-2-p-anisylpyrrole hydrochloride* formed yellow felted needles from methyl alcohol, probably containing 1MeOH of crystallisation. It decomposed without melting at 170° (Found : N, 8·0. $C_{17}H_{14}O_2N_2$,HCl requires N, 8·9%. $C_{17}H_{14}O_2N_2$,HCl,MeOH requires N, 8·1%).

E. *5-Amino-2 : 4-diphenylpyrrole.*—5-Nitroso-2 : 4-diphenylpyrrole (2·0 g.) in methyl alcohol (50 c.c.) was completely reduced catalytically with Adams's catalyst in 1½ hours, the hydrogen absorption being almost theoretical. The solution was filtered rapidly from the catalyst, and the alcohol distilled off, leaving a brown crystalline solid. Half of this was crystallised from benzene, but during the crystallisation the solution, and the stout needles which separated, became strongly blue. A sample dried in a vacuum had m. p. 155—156° (Found : C, 81·05; H, 6·4; N, 11·5. $C_{16}H_{14}N_2$ requires C, 82·0; H, 6·0; N, 12·0%). The other half of the crude amine was dissolved in acetic acid and refluxed for ½ hour with excess of acetic anhydride. The solution was poured on ice, giving a blue solid, which was collected, dissolved in alcohol, filtered from a little azamethine, treated with charcoal, filtered, and allowed to crystallise. The *acetyl* compound separated in bundles of short white needles, m. p. 171—172° (Found : C, 78·25; H, 5·6; N, 10·1. $C_{18}H_{16}ON_2$ requires C, 78·1; H, 5·8; N, 10·15%). This compound exists in at least two modifications, and a form, m. p. 192°, may be isolated; on long heating at 180°, the lower-melting is transformed into the higher-melting form.

The nitroso-compound was also reduced by zinc dust and acetic acid, but the amine was not obtained owing to the rapid formation of the azamethine during the working-up process.

F. *Formation of Azadipyrromethines by Condensation of 5-Nitroso-2 : 4-diarylpyrroles with 2 : 4-Diarylpyrroles.*—(a) *Condensation of 5-nitroso-2 : 4-diphenylpyrrole and 2 : 4-diphenylpyrrole.* Nitrosodiphenylpyrrole (1·25 g.) and diphenylpyrrole (1·1 g.) in acetic acid (25 c.c.) and acetic anhydride (5 c.c.) were heated on the steam-bath for ½ hour. The cooled mixture was filtered, the filtrate being practically colourless, and the residue of azamethine washed with acetic acid and methyl alcohol, and dried; yield, 2·15 g. (95%).

Condensation can also be effected without acetic anhydride, if the hydrochloride of the nitroso-compound is used, but the yields are less satisfactory.

(b) 2 : 2′ : 4-*Triphenyl-4′-p-anisylazadipyrromethine* (IX) *by two routes.* (1) A mixture of 5-nitroso-2 : 4-diphenylpyrrole hydrochloride (2·0 g.), 2-phenyl-4-*p*-anisylpyrrole (1·75 g.), and acetic acid (25 c.c.) was refluxed for 1 hour, kept for 16 hours, diluted with alcohol (25 c.c.), and filtered. The residue of *azamethine* crystallised from aqueous pyridine in small copper-coloured prisms, m. p. 256—257° (Found : C, 83·2; H, 5·1; N, 8·8. $C_{33}H_{25}ON_3$ requires C, 82·7; H, 5·05; N, 8·5%). (2) 5-Nitroso-2-phenyl-4-*p*-anisylpyrrole hydrochloride (2·0 g.) was condensed with diphenylpyrrole (1·2 g.) exactly as described under (1). The products of the two experiments were kindly examined by Dr. Bunn of I.C.I. (Alkali) Ltd., who reported that the *X*-ray diffraction patterns were identical.

G. *Action of Formamide and Ammonium Formate on Compounds related to γ-Nitro-β-phenylbutyrophenone.*—(1) Methyl γ-nitro-β-phenylpropyl ketone (Kohler and Drake, *J. Amer. Chem. Soc.*, 1923, **45**, 2147), when heated with formamide (3 parts) for ½ hour, gave a deep red-brown solution, and a brown oil which solidified on cooling. It could not be crystallised, nor did it show any of the typical reactions of the azamethine of the diphenylpyrrole series.

(2) γ-Nitro-αε-dibenzoyl-ββ-diphenylpentane, $NO_2$·CH(CHPh·$CH_2$·COPh)$_2$, was prepared by Worrall and Bradway's method (*J. Amer. Chem. Soc.*, 1936, **58**, 1607); only the higher-melting [230° (decomp.)] of the two forms claimed by these authors was obtained. During the preparation a considerable amount of blue colour developed, and, although no azamethine was isolated, traces of it were probably responsible for the colour. The dione itself gave no sign whatever of any blue colour with formamide or ammonium formate.

(3) γ-Nitro-β-phenylvalerophenone (Kohler, *J. Amer. Chem. Soc.*, 1916, **38**, 889) was obtained in the form, m. p. 101—103°. This gave no colour with ammonium formate.

(4) *γ-Nitro-β-phenylhexophenone*, made from α-nitropropane and chalkone by the method described by Kohler (*loc. cit.*) for the pentanone, was isolated in two forms; one had m. p. 156—158° (Found : C, 72·5; H, 6·35; N, 4·85. $C_{18}H_{19}O_3N$ requires C, 72·75; H, 6·4; N, 4·7%). This form was only slightly soluble in cold toluene, and crystallised from it in long needles. The other form, m. p. 88—90° (Found : N, 5·0%), was soluble in cold toluene and separated from *cyclo*hexane in clusters of short needles. Neither form gave any sign of coloured material on heating with formamide.

(5) When γ-nitrobutyrophenone (Reichert and Posmann, *Arch. Pharm.*, 1937, **275**, 75) was heated with formamide, the mixture became blue, greenish-blue, and finally red-brown. A red-brown amorphous solid which separated on cooling, was soluble in alcohol and insoluble in benzene, and bore no obvious relation to the tetraphenylazadipyrromethines. It was not further examined.

(6) *γ-Nitro-β-phenylbutyrophenoneoxime*, m. p. 108—110°, decomposed to a gum on storing (Found : N, 9·55. $C_{16}H_{16}O_3N_2$ requires N, 9·85%). It gave the azamethine readily with ammonium formate or with formamide. When solutions of the oxime in formic or acetic acid were evaporated, and the residues heated, considerable amounts of the azamethine were formed. A small quantity of the azamethine was also formed during the preparation of the oxime by the usual method.

(7) A detailed account of the action of formamide and ammonium formate on β-benzoyl-α-phenylpropionitrile (II, Ar = $Ar^1$ = Ph) and related compounds will be communicated later. At present it may be recorded that, whereas with ammonium formate this class of compound gives the azamethine (cf. p. 594), with formamide very little, or no blue colour is formed, and in its place a colourless compound is produced which gives the azamethine with ammonium formate and has been shown to be a formylated 5-amino-2 : 4-diphenylpyrrole.

H. *Action of Nitrogen Compounds, other than Formamide or Ammonium Formate, on the Nitrobutyrophenone.* (I, Ar = $Ar^1$ = Ph).—(1) *Ammonia.* The nitrobutyrophenone (0·5 g.) and aqueous ammonia (25 c.c., *d* 0·88) were heated in a Pyrex tube during 5 hours to 160—170°. When the tube was opened, there was no residual pressure and there remained a clear aqueous layer and a brown tar. From a solution of the latter in β-ethoxyethyl alcohol, after several hours, a small amount of the azamethine was gradually precipitated. When alcoholic ammonia was used in place of aqueous ammonia, a reddish tar was obtained, from which no blue compound was isolated.

(2) *Other agents.* The nitrobutyrophenone (I, Ar = $Ar^1$ = Ph) gave low yields of the azamethine on heating with urea or thiourea. No colour was formed on heating with acetamide, butyramide, or hexamethylenetetramine. With lauramide, a dull red colour was obtained. The formates of primary aliphatic amines (methylamine, benzylamine,

hexamethylenediamine) (cf. Novelli, *J. Amer. Chem. Soc.*, 1939, **61**, 520) gave the azamethine in low yield, but this was thought to be due to the liberation of ammonia by the strong heating of the formate; this is supported by the observation that aniline formate gave no colour. No colour was produced by the action of formodimethylamide.

I. *Degradation Reactions of 2 : 2′ : 4 : 4′-Tetra-arylazadipyrromethines.*—(1) *Hydriodic acid reduction.* The tetraphenylazamethine (III, Ar = Ar¹ = Ph) (0·5 g.) was refluxed with 65% hydriodic acid (25 c.c.) for ¾ hour; the blue colour was lost, and a dark solid formed. After cooling, the product was poured into water and the solid was collected, washed well, dissolved in alcohol, filtered, and poured slowly into a well-stirred solution of sodium thiosulphate. The light grey solid obtained was collected, washed, and dried. It crystallised from chloroform (charcoal) in steely-grey needles of 2 : 4-diphenylpyrrole, m. p. 177—179°, which did not depress the m. p. of an authentic specimen.

(2) *Potassium permanganate oxidation.* (a) *Neutral.* The azamethine (1·0 g.), potassium permanganate (2·0 g.), magnesium sulphate (2·0 g.), and water (100 c.c.) were rolled in a ball mill for 24 hours, and then kept for 48 hours. Excess of sodium bisulphite solution was added, and the mixture gently warmed (at this stage there was a distinct smell of benzaldehyde). The mixture was extracted with ether, and the purple solution dried with magnesium sulphate and decolorised with the minimum quantity of charcoal. On removal of the ether, an oil remained which rapidly solidified and was identified as benzoic acid (0·13 g.). (b) *Acid.* Acid oxidation was rapid; the decolorised solution was steam-distilled and an ethereal extract of the distillate gave benzoic acid.

Oxidation of 2 : 2′-diphenyl-4 : 4′-di-*p*-anisylazadipyrromethine, and of the isomer, 4 : 4′-diphenyl-2 : 2′-di-*p*-anisylazadipyrromethine (III; Ar¹ = Ph, Ar = $C_6H_4$·OMe; and Ar¹ = $C_6H_4$·OMe, Ar = Ph respectively) gave mixtures of acids, from which anisic acid was obtained in each case by crystallisation from water. These results provided confirmation that aryl groups in the nitrobutanone (I) did not take part in any cyclisation process, but remained as pendant aryl groups in the blue pigment.

(3) *Other degradations of* (III, Ar = Ar¹ = Ph). (*a*) With ceric sulphate complex results were obtained, and there were isolated, surprisingly, two aldehydes (or ketones) as their 2 : 4-dinitrophenylhydrazones, m. p. 156—157° and 159—160°; these depressed each other's m. p., but the latter compound did not depress the m. p. of acetaldehyde-2 : 4-dinitrophenylhydrazone. (*b*) With lead tetra-acetate in acetic acid or benzene, decoloration was rapid, but no crystalline product was obtained. (*c*) With hydroxylamine in pyridine, a crystalline product was obtained, $C_{32}H_{22}ON_2$. The nature of this compound will be discussed in a later communication. (*d*) Thionyl chloride in large excess decolorised the azamethine on boiling, but no crystalline product was obtained. (*e*) With concentrated nitric acid, complex yellow degradation products were obtained.

The author thanks Mr. C. Paine for constant encouragement and much valuable advice; also his many colleagues in the Research Department of I.C.I. (Dyestuffs) Limited, for help and advice; and I.C.I. (Dyestuffs) Limited for permission to publish this work.

I.C.I. (Dyestuffs) Limited, Manchester, 9. [*Received, April 28th*, 1943.]

---

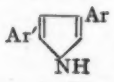
## 157. 2 : 4-*Diarylpyrroles. Part II. Methines.*

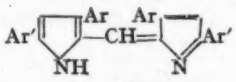
By Maurice A. Thorold Rogers.

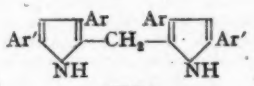
2 : 4-Diarylpyrroles readily form *methines* of type (II) either by condensation with ethyl orthoformate or other suitable agents, or by conversion into the *aldehyde* (IV) and further condensation with a second molecule of the diarylpyrrole. meso-*Phenylmethines* of type (V) have also been prepared. Metallic derivatives of the methines are described.

In Part I (preceding paper) the preparation of a new class of compound, the azadipyrromethines, from a new class of pyrrole, 2 : 4-diarylpyrroles, is described. A few of the reactions of diarylpyrroles for which there is some analogy in the alkylpyrrole series are now described.

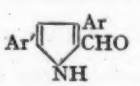
2 : 4-Diphenylpyrrole (I, Ar = Ar′ = Ph) condenses readily in acetic acid with ethyl orthoformate or with diphenylformamidine (Imperial Chemical Industries, Ltd., Piggott, and Rodd, B.P. 344,409, 354,898. No intermediate of the type there described was obtained) to give the red, crystalline *methine* (II, Ar = Ar′ = Ph). The same methine is formed from the pyrrole and formic acid, or formaldehyde in the presence of air. The methane (III) is presumably very unstable, as it has not been isolated.

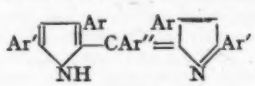

(I.)

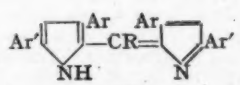

(II.)


(III.)

The same methine was made very readily from the *aldehyde* (IV) by condensation with one molecule of (I). The aldehyde (IV) has been very conveniently prepared by the methylformanilide–phosphorus oxychloride method (Vilsmeier and Haak, *Ber.*, 1927, **60**, 119; cf. Fieser, *Org. Synth.*, XX, 11; B.P. 311,208, 343,570, 456,534, and 524,696)—apparently its first application to the pyrrole series.


(IV.)


(V.)


(VI.)

With benzotrichloride, the pyrrole (I) condenses readily in acetic acid to give meso-*phenylmethines* of type (V). The same product is obtained by condensing benzoic acid with the pyrrole in, for example, phosphorus oxychloride. As might be expected, the *meso*-phenylmethine is most sensitive to pH.

Diarylpyrroles dissolve in hot acetic acid, and the solution becomes blue on boiling. There is little doubt that this colour can be attributed to the *meso*-alkyl-methine (VI).

The *copper* complex of the methine (II) was of the normal type, 2 methine = 1 Cu; but the copper complex from the *meso*-phenylmethine, a somewhat intractable compound, appeared to be of the type 1 methine = 1 Cu.

This work is the subject of pending patent applications.

## Experimental.

Analyses by Mr. E. S. Morton. M. p.'s are uncorrected.

2:2′:4:4′-*Tetraphenyldipyrromethine* (II, Ar = Ar′ = Ph).—(1) 2:4-Diphenylpyrrole (4·0 g.) in acetic acid (50 c.c.) was refluxed with ethyl orthoformate (3 c.c.); the solution almost immediately became intensely crimson, and soon set to a crystal paste. After cooling, the crystals were collected, washed with acetic acid and with methyl alcohol, and dried (3·5 g.). The *methine* crystallised from nitrobenzene in red needles, m. p. 284—286° (Found: C, 88·65; H, 5·3; N, 6·4. $C_{33}H_{24}N_2$ requires C, 88·4; H, 5·35; N, 6·25%). (2) Similar yields were obtained by refluxing diphenylpyrrole (5·0 g.), acetic anhydride (25 c.c.), and diphenylformamidine (4·5 g.) for 1 hour.

2:4-*Diphenylpyrrole-5-aldehyde*.—A mixture of methylformanilide (24 c.c.) and phosphorus oxychloride (105 c.c.) was kept at room temperature for 1 hour, then cooled below 5°, and the pyrrole (20 g.) added during 1 hour. The mixture was stirred below 5° for 2 hours, allowed to warm to room temperature, and poured on ice, with agitation; the phosphorus oxychloride decomposed, leaving a red gum. At 50° the gum hydrolysed with formation of a yellow solid. This was collected, washed with aqueous sodium acetate and with water, and dried at 40°; the *aldehyde* crystallised from toluene in short, biscuit-coloured or pink needles. It was purified for analysis by recrystallisation from toluene, giving white needles, m. p. 187—188° (Found: C, 82·55; H, 5·0; N, 5·8. $C_{17}H_{13}ON$ requires C, 82·6; H, 5·25; N, 5·65%). On strong heating the aldehyde formed a red mass, probably containing the methine.

It formed an *oxime*, fluffy white needles from toluene, m. p. 202° (slow decomp.), which was probably a mixture of two forms (Found: C, 77·85; H, 5·05; N, 10·75. $C_{17}H_{14}ON_2$ requires C, 77·85; H, 5·35; N, 10·7%). With *p*-nitrophenylhydrazine in acetic acid it formed a p-*nitrophenylhydrazone*, dark red, saw-edged needles, m. p. 241—242° (sintering at 235°) from acetic acid (Found: N, 14·25. $C_{23}H_{18}O_2N_4$ requires N, 14·7%). Condensed with 2:4-dinitrotoluene (0·9 g.) and piperidine (3 drops), the aldehyde (1·25 g.) gave, after 1 hour at 130° and 3 hours at 170°, α-(2:4-*dinitrophenyl*)-β-(2:4-*diphenyl-5-pyrrolyl*)*ethylene*, dark hair-like needles, m. p. 254—255°, from moist pyridine or from butanol (Found: N, 10·35. $C_{24}H_{17}O_4N_3$ requires N, 10·0%).

Catalytic reduction of the aldehyde (Raney nickel in methanol) readily gave 2:4-*diphenylpyrrole-5-carbinol*, which was very unstable. With acids, or even on long standing, or on heating, it gave the methine, with loss of formaldehyde (smell and dinitrophenylhydrazone). It was recrystallised from benzene; m. p. 170° (decomp.) approx. (Found: C, 81·85; H, 5·8. $C_{17}H_{15}ON$ requires C, 82·0; H, 6·05%). An attempt to acylate the carbinol with acetic anhydride in pyridine resulted in the formation of the methine.

2-*Phenyl*-4-p-*anisylpyrrole-5-aldehyde*, prepared from the corresponding pyrrole (this vol., p. 594) exactly as described for diphenylpyrrolealdehyde, formed white felted needles from toluene, m. p. 158—159°, turning red on strong heating (Found: C, 78·1; H, 5·5. $C_{18}H_{15}O_2N$ requires C, 78·0; H, 5·4%). It gave an *oxime*, m. p. 196—198°, from toluene, which was obviously a mixture of *syn*- and *anti*-forms, as both long, hair-like and short thick needles were visible (Found: C, 74·25; H, 5·5. $C_{18}H_{16}O_2N_2$ requires C, 74·0; H, 5·5%).

2:2′:4-*Triphenyl*-4′-p-*anisyldipyrromethine*.—Diphenylpyrrolealdehyde (1·0 g.) and 2-phenyl-4-*p*-anisylpyrrole (1·0 g.) were refluxed with acetic acid (20 c.c.) and acetic anhydride (5 c.c.). After 1 hour the liquid was poured into water, and the product dried; it crystallised from aqueous pyridine in fiery copper-coloured platelets, m. p. 240—247° (Found: C, 85·4; H, 5·1; N, 6·0. $C_{34}H_{26}ON_2$ requires C, 85·4; H, 5·45; N, 5·85%).

*Copper Bis*-(2:2′:4:4′-*tetraphenyldipyrromethine*).—The methine (1·0 g.) in butanol (50 c.c.) was refluxed with copper acetate (0·5 g.). The crimson colour was replaced by magenta and platelets with a coppery sheen were formed. These were collected, and crystallised from pyridine–methyl alcohol (Found: C, 82·7; H, 4·45; N, 6·15; Cu, 6·35. $C_{66}H_{46}N_4Cu$ requires C, 82·9; H, 4·6; N, 5·85; Cu, 6·65%).

2:2′:4:4′-*Tetraphenyl*-meso-*phenyldipyrromethine*.—(1) Diphenylpyrrole (1·0 g.), benzotrichloride (1·0 c.c.), and acetic acid (25 c.c.) were refluxed for 1 hour, and the blue solution poured into water. This was made alkaline with sodium hydroxide and kept overnight. The solid product was collected and dried; it crystallised from β-ethoxyethyl alcohol in brown-red flattened needles, m. p. 268—270° (Found: C, 88·8; H, 5·2; N, 5·7. $C_{39}H_{28}N_2$ requires C, 89·3; H, 5·35; N, 5·35%).

(2) Diphenylpyrrole (4·4 g.) was dissolved in phosphorus oxychloride (20 c.c.), and benzoic acid (1·3 g.) added. The mixture was warmed on the steam-bath for 1 hour, cooled, poured on ice, and, when the phosphorus oxychloride had decomposed, heated to boiling. The coppery tar was washed by decantation and dissolved in the minimum quantity of alcohol, and the bright green solution poured into dilute sodium hydroxide solution. The red solid was collected, washed with water, dried, and crystallised from β-ethoxyethyl alcohol; yield, quantitative.

The meso-*phenylmethine* showed remarkable colour sensitivity to a variety of factors. Its solutions were generally red in alkaline and green in acid conditions; but a red ethereal solution of the base with a little acetic, formic or benzoic acid showed no change until the ether was allowed to evaporate on, for example, filter-paper. As the solvent evaporated, the colour became bright green. Spotting with ether gave a red mark, but methyl alcohol gave no change in colour. Other solvents showed intermediate, purplish, colour changes. Even the vapour of ether immediately and reversibly turned such a green test paper a dull purple.

*Copper* 2:2′:4:4′-*Tetraphenyl*-meso-*phenyldipyrromethine*.—The methine (0·5 g.), copper acetate (0·25 g.), and butyl alcohol (35 c.c.) were refluxed for 1 hour. A purple colour was formed, and the solution gradually became bluer and paler, and a mass of small prisms separated. These were collected, and crystallised with difficulty from nitrobenzene–methanol, giving needles (Found: C, 79·55; H, 5·0; N, 5·1; Cu, 9·85. $C_{39}H_{27}N_2Cu$ requires C, 79·9; H, 4·6; N, 4·8; Cu, 10·7. $C_{78}H_{54}N_4Cu$ requires C, 84·3; H, 4·85; N, 5·05; Cu, 5·75%).

The author thanks I.C.I. (Dyestuffs) Limited for permission to publish this work.

I.C.I. (Dyestuffs) Ltd., Manchester, 9. [*Received, April 28th*, 1943.]

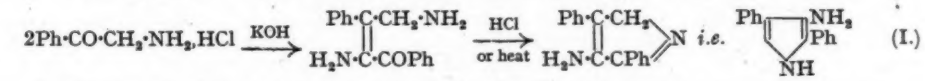
## 158. 2 : 4-*Diarylpyrroles. Part III.* 3-*Amino*-2 : 4-*diphenylpyrrole.*

By Maurice A. Thorold Rogers.

The blue compound obtained by Gabriel by the action of benzaldehyde and air on 3-amino-2 : 4-diphenylpyrrole (I) is shown to have the structure (III). Benzoylation of (I) under Schotten–Baumann conditions gave 3-benzamido-2 : 4-diphenylpyrrole (IV) and a red compound, shown to be 3 : 3′-dibenzamido-2 : 2′ : 4 : 4′-tetraphenyl-*meso*-phenyldipyrromethine (V) by synthesis from (IV) and benzotrichloride.

The interesting properties of 2 : 4-diarylpyrroles discussed in Parts I and II (preceding papers) led to a search for earlier examples of diarylpyrroles of this orientation. The only recorded cases are 3-amino-2 : 4-diphenylpyrrole * (Gabriel, *Ber.*, 1908, **41**, 1138) and its derivatives, and the *p*-tolyl analogue (Rüdenburg, *Ber.*, 1913, **46**, 3558).

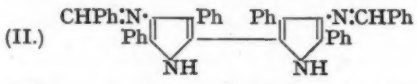
Gabriel's synthesis left some doubt whether the compound was a pyrrole, and Gabriel himself used the alternative name " bisanhydro-phenacylamine "; the synthesis was

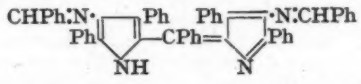


(I.)

The present work leaves little doubt that the pyrrole structure is correct.

In the first place, Gabriel described the formation of an intensely blue compound (" Gabriel's blue ") when the pyrrole (I) was heated with benzaldehyde in a stream of air. He did not give an exact structural formula, but inferred that the blue compound was represented by (II), though he noted that the nitrogen analyses were unsatisfactory. Repetition of the work has shown that in fact it was the carbon analysis which was unsatisfactory, and new analyses are in good agreement with the more probable structure (III).

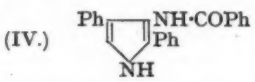


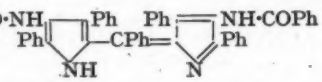



(III.)

Confirmation of these analyses was obtained by using anisaldehyde in place of benzaldehyde; Zeisel determination of methoxy-groups showed conclusively that three aldehyde residues were incorporated in " Gabriel's blue." Both compounds showed the sensitivity of colour to pH expected of a *meso*-phenylmethine (preceding paper).

Gabriel described the benzoylation of (I) under Schotten–Baumann conditions. It has now been found more convenient to prepare the benzoyl compound (IV) by acylation with benzoyl chloride in pyridine; for under Schotten–Baumann conditions a bright red compound is also formed, to which the structure (V) was attributed.



(V.)

This structure has been confirmed by independent synthesis from the benzoyl compound (IV) and benzotrichloride (cf. preceding paper).

This work is the subject of pending patent applications.

### Experimental.

Analyses are by Mr. E. S. Morton. M. p.'s are uncorrected.

3-*Amino*-2 : 4-*diphenylpyrrole* (I).—This was made according to Gabriel's instructions (*loc. cit.*). It was found inadvisable to attempt to purify the " Monoanhydrophenacylamine " by recrystallisation from benzene, as considerable decomposition resulted; the crude material was quite satisfactory for conversion into the hydrochloride of (I).

" *Gabriel's Blue.*"—The table shows the analyses obtained by the present author, and the figures calculated for Gabriel's formula (II) and for the *meso*-phenylmethine formula (III) now favoured.

| | Found. | | Required. | |
|---|---|---|---|---|
| | Gabriel. | Present work. | II, $(C_{23}H_{17}N_2)_2$. | III, $C_{53}H_{36}N_4$. |
| C, % ..... | 85·74 | 87·3 | 86·0 | 87·4 |
| H, % ..... | 5·37 | 5·65 | 5·3 | 4·9 |
| N, % ..... | 7·78 | 7·55 | 8·7 | 7·7 |

" Gabriel's blue " is therefore given the constitution : 3 : 3′-*dibenzylideneamino*-2 : 2′ : 4 : 4′-*tetraphenyl*-meso-*phenyldipyrromethine* (III).

3 : 3′-(*Di*-p-*anisylideneamino*)-2 : 2′ : 4 : 4′-*tetraphenyl*-meso-p-*anisyldipyrromethine* (" Methoxy-Gabriel's blue ").—3-Amino-2 : 4-diphenylpyrrole (0·6 g.) and anisaldehyde (3 c.c.) were heated under reflux in the steam-bath in a slow stream of air. The product was triturated with methyl alcohol, and the dark residue recrystallised from nitrobenzene [Found: N, 6·95; OMe, 11·85. $C_{53}H_{32}N_4(OMe)_2$ requires N, 6·85; OMe, 11·35%].

3-*Benzamido*-2 : 4-*diphenylpyrrole* (IV).—(1) *As described by Gabriel, under Schotten–Baumann conditions.* When reaction was complete, the benzene was distilled off, and the reddish solid residue collected and dried. It was

* Fischer and Orth (" Chemie des Pyrroles," 1934, Vol. I, p. 112) give a second reference, F. Angelico and A. Angeli, R.A.L. (5), **14**, I, 701 (1905); reference to the abstract (*Centr.*, 1905, II, 900) shows that the compound referred to is 3-amino-2 : 5-diphenylpyrrole.

extracted with alcohol, leaving a small scarlet residue which was shown to be identical with (V) prepared from benzotrichloride. From the alcoholic filtrate greenish prisms were obtained, m. p. 220—222° (Gabriel gives m. p. 218—219°); 0·5 g. from 2·0 g. of the base.

(2) *In pyridine.* To 3-amino-2 : 4-diphenylpyrrole (2·0 g.) in pyridine (25 c.c.) was added benzoyl chloride (3 c.c.) dissolved in pyridine (15 c.c.). The mixture became warm; after an hour it was poured into water, and made alkaline with sodium carbonate. The solid, recrystallised from alcohol, formed biscuit-coloured prisms (2·25 g.), m. p. 222—223°.

3 : 3′-*Dibenzamido*-2 : 2′ : 4 : 4′-*tetraphenyl*-meso-*phenyldipyrromethine* (V).—3-Benzamido-2 : 4-diphenylpyrrole (1·15 g.) in acetic acid (15 c.c.) was refluxed with benzotrichloride (0·75 g.) for 1 hour, the mixture cooled, and the blue-green solution poured into dilute sodium hydroxide solution. The purple precipitate was collected, dried, and crystallised from nitrobenzene containing a trace of triethylamine, sufficient to form a deep red solution. On cooling, the meso-*phenylmethine* crystallised in short scarlet needles, m. p. 345° (decomp.) (Found: C, 82·55; H, 4·95; N, 7·55. $C_{53}H_{38}O_2N_4$ requires C, 83·3; H, 5·0; N, 7·35%).*

The author thanks I.C.I. (Dyestuffs) Limited for permission to publish this work.

I.C.I. (Dyestuffs) Ltd., Manchester, 9. [*Received, April 28th*, 1943.]

---

## 159. *Studies in the Sterol Group. Part XLV. Investigation of the Homogeneity of Sitosterol by Oxidation with the Oppenauer Reagent.*

By D. H. R. Barton and E. R. H. Jones.

Oxidation of Tall-öl sitosterol by Oppenauer's method, followed by careful chromatographic purification, gives pure $\Delta^4$-β-sitostenone, m. p. 88°. Similar treatment of sitosterol from wheat-germ oil indicates that this material is far from homogeneous, although the main product is the same $a\beta$-unsaturated ketone. Wheat-germ sitosterol contains triacontane. Rather surprisingly, the small amount of saturated sterol present in both samples of sitosterol is oxidised to sitostanone.

Oppenauer oxidation, followed by chromatographic analysis of the ketones, has been shown to be of considerable value for examining the homogeneity of sitosterols, and in particular, for determining approximately the proportion of sitostanol present. It provides a far more delicate and convenient criterion of purity than the fractional crystallisation method employed hitherto and would appear to be generally applicable in the steroid field.

It was recently observed (Jones, Wilkinson, and Kerlogue, J., 1942, 391) that a specimen of β-sitosterol, with constants in good agreement with those reported in the literature, was actually far from homogeneous. The method described has now been examined in more detail with Tall-öl sitosterol (for the gift of a sample of which we are deeply indebted to Professor R. E. Marker of the Pennsylvania State College), which is reputed to contain a high percentage of the β-isomer (Sandqvist and Bengtsson, *Ber.*, 1931, **64**, 2167; see also Windaus, Werder, and Gschaider, *Ber.*, 1932, **65**, 1006).

Tall-öl sitosterol (m. p. 137—138°, $[\alpha]_D^{20°}$ −28·7°) was oxidised by Oppenauer's method (*Rec. Trav. chim.*, 1937, **56**, 137), and the crude ketone carefully chromatographed (" flowing chromatogram ") on a column of alumina. It should be noted that much larger columns than usual were used in the experiments described in this paper, since reasonably good separations could only be achieved by using 100 times as much adsorbent as adsorbate. The results illustrated in Fig. 1 indicate that the oxidation product consists of four main portions, which for convenience are designated A, B, C, and D.

A, which accounted for 3% of the theoretical yield of ketonic material, was collected in four fractions with m. p.'s 113—100°, and will be discussed later. A second chromatographic analysis of B (three fractions of m. p.'s 155—152°), isolated in 2·5% yield, gave sitostanone, m. p. 157°.

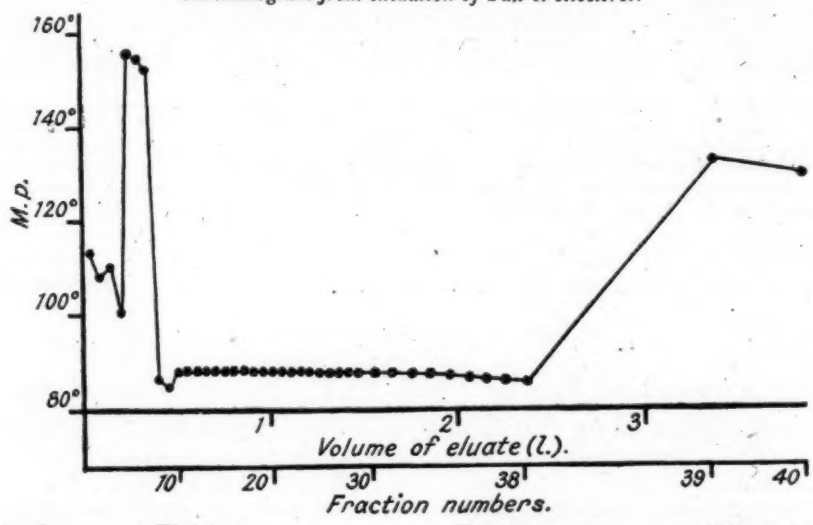
The main product of the oxidation, portion C, was represented by 32 fractions, m. p.'s 88—85°, which amounted to 66% of the theoretical yield, and consisted mainly of $\Delta^4$-β-sitostenone. Fractions 10—13, which had m. p. 88° and $[\alpha]_D^{20°}$ +85·8°, were repeatedly recrystallised and rechromatographed without undergoing the slightest change in m. p. or rotation and must be pure $\Delta^4$-β-sitostenone (cf. Marker and Wittle, *J. Amer. Chem. Soc.*, 1937, **59**, 2704; Marker, Kamm, and Wittle, *ibid.*, 1938, **60**, 1072; Heiduschka and Gloth, *Arch. Pharm.*, 1915, **253**, 415; Coffey, Heilbron, and Spring, J., 1936, 738). The highest m. p. previously recorded for the ketone is 83—84° (Jones, Wilkinson, and Kerlogue, *loc. cit.*). The m. p.'s of the oxime, semicarbazone, and 2 : 4-dinitrophenylhydrazone did not differ appreciably from those already recorded, but the intensities of the light absorption of both the ketone and its derivatives were somewhat higher than those obtained previously. Although the major portion (C) of the oxidation product of Tall-öl sitosterol undoubtedly consists of $\Delta^4$-β-sitostenone, there was a slight but definite indication that the later fractions were contaminated with small amounts of a closely related sitostenone, since rechromatography yielded a sitostenone with m. p. 86° and $[\alpha]_D^{20°}$ +89·0°.

The unoxidised sterol, which comprised portion D, had m. p. 135—136°, $[\alpha]_D^{20°}$ −19·0°, indicating that no marked concentration of the strongly dextrorotatory sitostanol had occurred. This unexpected finding is further discussed below.

* Throughout the work on diarylpyrroles a tendency has been found for carbon analyses to be low. Compare analyses for diphenylpyrrole itself (this vol., p. 594) and Gabriel's analytical results (p. 598).

FIG. 1.

*Chromatogram from oxidation of Tall-öl sitosterol.*

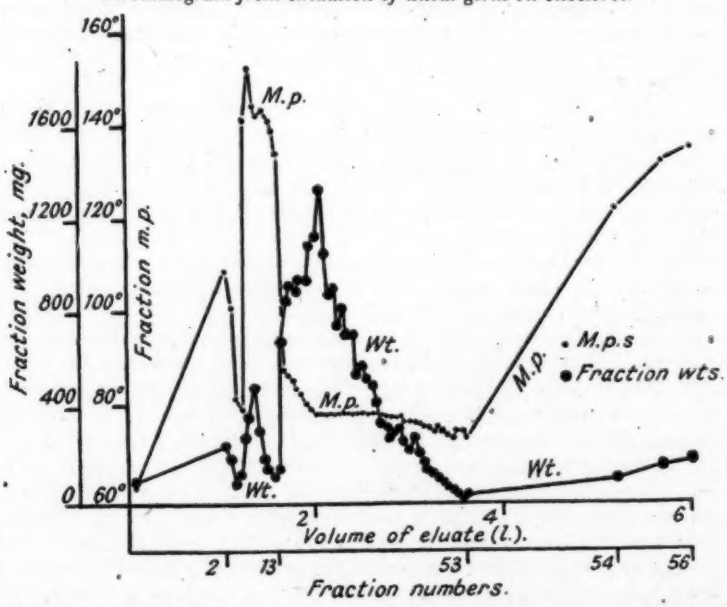



| Fraction numbers. | Elutriant. | | Fraction numbers. | Elutriant. | |
|---|---|---|---|---|---|
| 1—4 | Benzene . . . | A | 31—38 | 95 Benzene : 5 Ether . | C |
| 5—7 | Benzene . . . | B | 38—39 | Ether . . . . | — |
| 8—30 | 97½ Benzene : 2½ Ether . | C | 39—40 | Methyl alcohol . . | D |

The chromatogram obtained when the above procedure was repeated with wheat-germ oil sitosterol is illustrated in Fig. 2, and is seen to be conveniently divisible into five sections, designated E, F, G, H, and I. E was easily eluted from the column with light petroleum, and crystallisation gave triacontane in 0·3% yield.

FIG. 2.

*Chromatogram from oxidation of wheat-germ oil sitosterol.*




| Fraction numbers. | Elutriant. | | Fraction numbers. | Elutriant. | |
|---|---|---|---|---|---|
| 1 | Light petroleum . | E | 14—53 | 90 Benzene : 10 Ether . | H |
| 2—5 | Benzene . . . | F | 53—54 | Ether . . . . | — |
| 6—13 | 95 Benzene : 5 Ether . | G | 54—56 | Methyl alcohol . . | I |

It was also obtained by chromatography of the original sterol. This hydrocarbon has frequently been isolated from plant sources, and Ichiba (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1935, **28**, 112) obtained an impure hydrocarbon from wheat-germ sitosterol.

Further elution gave a 1·8% yield of fractions (F), with m. p.'s varying from 110° to 80°. Rechromatography and crystallisation of this material, essentially similar to the corresponding fractions (A) isolated from Tall-öl sitosterol, failed to give any pure substance, and the poor yields precluded a more detailed examination. It was ascertained, however, that the main constituent is probably an αβ-unsaturated ketone, and one fraction exhibited intense absorption in the ultra-violet ($E^{1\%}_{1\,cm.}$ at 2400 A. = 365). Chromatographic examination failed to reveal the presence of any similar material in the original sterol.

Sitostanone (6% yield) was isolated without difficulty from the eight fractions (m. p.'s 152—136°) comprising portion G of the chromatogram. It was ascertained by chromatographic analysis that neither of the original sterols contained any sitostanone. Since it is well recognised that saturated sterols are not readily oxidised under the standard Oppenauer conditions (Jones, Wilkinson, and Kerlogue, *loc. cit.*; Reich and Reichstein, *Arch. Intern. Pharm. Ther.*, 1941, **65**, 415), it can only be concluded that the oxidation of the sitostanol present in the starting materials is brought about by the intervention of the αβ-unsaturated ketone, which must act as a powerful hydrogen acceptor.

The main ketonic portion (H), consisting of 40 fractions with m. p.'s varying from 88° to 75°, representing a 69·5% yield, was by no means as homogeneous as that obtained from Tall-öl sitosterol. Repeated rechromatography resulted in the isolation in a pure state of only Δ⁴-β-sitostenone, m. p. 88°, $[\alpha]_D^{20°}$ +85·9°, identical in all respects with that obtained from the alternative source. The accompanying ketones appeared to be αβ-unsaturated and, as was observed with the ketones from Tall-öl sitosterol, had somewhat higher rotations than the pure Δ⁴-β-sitostenone. After recrystallisation, the unchanged sterol (I) (1·5% yield) had m. p. 134·5—135·5°, $[\alpha]_D^{20°}$ −24·1°, and, like the material recovered in the previous experiment, showed little evidence of increased content of saturated sterol (sitostanol).

Although the method now described has led to the isolation of only one pure sitostenone, it furnishes, nevertheless, an excellent means of ascertaining the degree of homogeneity of a sitosterol, a process far more convenient and reliable than the tedious fractional crystallisation methods hitherto employed. The value of the results obtained is clearly illustrated in the accompanying table. The total yields based on the original

| | Wheat-germ oil sitosterol. | | Tall-öl sitosterol. | |
|---|---|---|---|---|
| | Yield, %, based on original sterol. | Proportion of ketonic product, %. | Yield, %, based on original sterol. | Proportion of ketonic product, %. |
| Triacontane | 0·3 | 0·4 | — | — |
| Unidentified ketone, m. p. *ca.* 115° | 1·8 | 2·3 | 3·2 | 4·5 |
| Sitostanone | 5·9 | 7·6 | 2·5 | 3·2 |
| Sitostenones | 69·5 | 89·7 | 66·2 | 92·3 |
| Recovered sterol | 1·5 | — | 3·8 | — |

sterol do not total 100%, a discrepancy occasioned by the inevitable losses incurred in the crystallisation of each fraction from the chromatogram.

## Experimental.

M. p.'s are uncorrected. Rotations were measured in a 1-dcm. tube in chloroform solutions, made up in carefully calibrated flasks. Specimens for analysis were dried at a suitable temperature in a high vacuum for some hours. Chromatogram fractions were all crystallised from either methyl or ethyl alcohol before determination of the m. p. Except where stated otherwise, light petroleum refers to that fraction of b. p. 40—60°.

*Oxidation of Tall-öl Sitosterol.*—To a solution of the commercial sterol [10 g.; m. p. 137—138°, $[\alpha]_D^{20°}$ −28·7° (*c* = 5·030)] in dry benzene (300 c.c.) and dry acetone (120 c.c.), freshly sublimed aluminium *tert.*-butoxide (12 g.) was added, and the mixture refluxed for 18 hours. The resulting solution was washed repeatedly with dilute sulphuric acid and water, and the benzene distilled off; the residue, after being heated for 2 hours at 100° in a vacuum to remove mesityl oxide, readily solidified on cooling. This residue was dissolved in light petroleum and chromatographed on a 3·6 × 150 cm. column of " Birlec " alumina (see Fig. 1).

Portion A (323 mg.) was not investigated further. Portion B (249 mg.) was rechromatographed on a 3·0 × 40 cm. column of the same adsorbent and readily yielded sitostanone, m. p. 157°, unchanged on repeated recrystallisation from alcohol (Found: C, 83·6; H, 12·1. Calc. for $C_{29}H_{50}O$: C, 84·0; H, 12·1%). This exhibited no high-intensity absorption in the ultra-violet, and gave a yellow 2 : 4-*dinitrophenylhydrazone*, m. p. 223° (decomp.) (Found: N, 9·1. $C_{35}H_{54}O_4N_4$ requires N, 9·4%).

From C (6·62 g.), fractions 10—13 were combined and repeatedly crystallised, without any change in m. p., giving pure Δ⁴-β-sitostenone, m. p. 88°, $[\alpha]_D^{20°}$ +85·8° (*c* = 4·475). The analytical data for the ketone and its derivatives, prepared in the usual manner, are given in the following table.

| | | | Found, %. | | | Calc., %. | | |
|---|---|---|---|---|---|---|---|---|
| Substance. | M. p. | Formula. | C. | H. | N. | C. | H. | N. |
| Δ⁴-β-Sitostenone | 88° | $C_{29}H_{48}O$ | 84·4 | 11·7 | — | 84·4 | 11·7 | — |
| Oxime | 175·5 | $C_{29}H_{49}ON$ | 81·45 | 11·7 | — | 81·45 | 11·55 | — |
| | | | 81·45 | 11·5 | — | — | — | — |
| Semicarbazone | 250 * | $C_{30}H_{51}ON_3$ | 76·7 | 10·8 | — | 76·7 | 10·9 | — |
| 2 : 4-Dinitrophenylhydrazone | 253 * | $C_{35}H_{52}O_4N_4$ | — | — | 9·35 | — | — | 9·45 |

* With decomposition.

Light-absorption data for the ketone and its derivatives were as follows:

| Substance. | $\lambda_{max.}$, A. | $\varepsilon_{max.}$ | Solvent. | Substance. | $\lambda_{max.}$, A. | $\varepsilon_{max.}$ | Solvent. |
|---|---|---|---|---|---|---|---|
| Δ⁴-β-Sitostenone | 2405 | 20,000 | EtOH | Semicarbazone | 2730 | 30,000 | $CHCl_3$ |
| Oxime | 2410 | 23,500 | " | 2 : 4-Dinitrophenylhydrazone | 3890 | 32,000 | " |

The last 7 fractions of portion C were combined and rechromatographed on a 3·0 × 40 cm. column of alumina;

14 fractions were collected, the last 4 of these being recrystallised twice from aqueous methyl alcohol, giving a ketone with m. p. 86°, $[\alpha]_D^{20°}$ +89·0° ($c$ = 3·950).

The two fractions of unchanged sterol comprising portion D (383 mg.) were combined, and on recrystallisation from alcohol had m. p. 135—136°, $[\alpha]_D^{20°}$ −19·0° ($c$ = 1·870).

*Chromatography of Tall-öl Sitosteryl Acetates.*—The crude acetates [10 g.; m. p. 118·5—119·5°, $[\alpha]_D^{20°}$ −33·0° ($c$ = 8·485)], prepared with acetic anhydride and pyridine, were adsorbed and fractionally eluted from a 3·1 × 105 cm. column of "Birlec" alumina, 14 fractions with m. p.'s ranging from 122° to 114° being obtained. None of these fractions was pure, for on repeated crystallisation the m. p. slowly rose and the rotations changed.

*Oxidation of Wheat-germ Oil Sitosterol.*—The crude sterol {30 g.; m. p. 137—138°, $[\alpha]_D^{20°}$ −26·6 ($c$ = 14·11)} was oxidised as described above, and the product, which solidified on cooling, was dissolved in light petroleum and chromatographed, giving the results illustrated in Fig. 2. After several recrystallisations from alcohol–benzene, the triacontane (98 mg.) had m. p. 65° (lit., m. p. 65°) (Found: C, 85·2; H, 14·9. Calc. for $C_{30}H_{62}$: C, 85·3; H, 14·7%).

Portion F (554 mg.), corresponding to A from the Tall-öl chromatogram, was rechromatographed on a 3·0 × 40 cm. column, giving 7 fractions with m. p.'s ranging from 115—116° to 97—98°, all of which gave red precipitates with an acid solution of 2 : 4-dinitrophenylhydrazine. The second fraction, the only one so examined, exhibited high-intensity light absorption (see p. 601). Unfortunately, none of the fractions was homogeneous, the m. p.'s rising on further chromatography or recrystallisation.

Rechromatography of G (1·78 g.) on a 3·1 × 105 cm. column gave 11 fractions, and pure sitostanone, identical with the material described above, was readily obtained.

The 40 fractions (20·85 g.) comprising portion H were chromatographed twice more in three groups on 2·9 × 45 cm. columns, whereby a total of 78 fractions was obtained. Only one pure substance, however, *viz.*, $\Delta^4$-$\beta$-sitostenone, was isolated by this procedure. It had m. p. 88°, $[\alpha]_D^{20°}$ +85·9° ($c$ = 2·070), which constants remained unchanged after repeated crystallisation, and it gave the same derivatives as the ketone already described. Crystallisation of any of the remaining fractions from these chromatographic experiments invariably resulted in an increase in the m. p. Two typical fractions had the following constants: (*a*) m. p. 85°, $\varepsilon_{max.}$ at 2405 A. = 19,500; (*b*) m. p. 80°, $[\alpha]_D^{20°}$ +88·8° ($c$ = 2·605), $\varepsilon_{max.}$ at 2405 A. = 19,500.

The last fraction of the unchanged sterol (I) (461 mg.) had m. p. 134·5—135·5°, $[\alpha]_D^{20°}$ −24·1°.

The authors thank Professor I. M. Heilbron, D.S.O., F.R.S., for his interest in the work described in this and the following paper. They are indebted to the Rockefeller Foundation for financial assistance, and one of them (D. H. R. B.) gratefully acknowledges a grant from the Department of Scientific and Industrial Research. Thanks are also due to Professor R. E. Marker and Glaxo Laboratories Ltd. for gifts of sitosterol.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W. 7. [*Received, July, 29th,* 1943.]

---

## 160. *Studies in the Sterol Group. Part XLVI. The Isolation of a New Form of $\Delta^4$-Cholestenone.*

By D. H. R. BARTON and E. R. H. JONES.

Oxidation of cholesterol by Oppenauer's method and careful chromatographic analysis of the product gives $\Delta^4$-cholestenone in two forms, m. p.'s 88° and 82°. They are interconvertible and give ketonic derivatives with identical m. p.'s. The optical rotations and light-absorption intensities of both forms are slightly higher than those previously recorded.

CHOLESTEROL has been oxidised to $\Delta^4$-cholestenone by Oppenauer's method (*Rec. Trav. chim.*, 1937, **56**, 137) by a number of workers and in each case the m. p. recorded has been in the range 80—82°. Recently one of us (Jones, Wilkinson, and Kerlogue, J., 1942, 391) prepared the ketone in this manner and reported m. p. 81—82°. The experience gained in chromatographic analysis (see previous paper) induced us to repeat this work, with the result that on careful chromatography of the crude $\Delta^4$-cholestenone, two different forms, m. p.'s 88° and 82°, were isolated. Their optical rotations and light-absorption intensities (see table) are identical, and they give the same semicarbazone and 2 : 4-dinitrophenylhydrazone.

The haphazard manner in which fractions of different m. p.'s were isolated from the chromatogram (see Experimental) suggested that they might be interconvertible, and this was readily established. A mixture of the two forms has m. p. 88°, and samples which melt at 82° when cooled and reheated often have m. p. 88°. In general, both forms can be recrystallised from alcohol without undergoing conversion, but occasionally the form of m. p. 82° gave the higher-melting form on crystallisation. It is probably purely fortuitous that the converse change has never been noted, for if a saturated alcoholic solution of either of the two forms is seeded with the other form, then in every case the form with m. p. corresponding to the seeding crystals is deposited. Thorough drying in high vacuum failed to alter the constants of either form, and this and the facts recorded above preclude the possibility that the phenomena observed can be explained by hydrate or alcoholate formation.

*Constants of $\Delta^4$-cholestenone.*

| Reference. | M. p. | $[\alpha]_D^{20°}$ in $CHCl_3$. | $\varepsilon_{max.}$ in EtOH. |
|---|---|---|---|
| Diels and Abderhalden, *Ber.*, 1904, **37**, 3092 | 78° | — | — |
| Windaus, *Ber.*, 1906, **39**, 518 | 81—82 | — | — |
| Heilbron and Sexton, J., 1928, 347, 2825 | 80 | — | — |
| Menschick, Page, and Bossert, *Annalen*, 1932, **495**, 227 | — | — | 16,200 |
| Grasshof, *Z. physiol. Chem.*, 1934, **223**, 249 | — | +83·5° | — |
| Butenandt and Wolff, *Ber.*, 1935, **68**, 2091 | 79—80 | +88·6 | — |
| Mohler, *Helv. Chim. Acta*, 1937, **20**, 289 | — | — | 15,000 |
| Galinovsky, *Ber.*, 1941, **74**, 1048 | 80—81 | +88·7 | — |
| Jones, Wilkinson, and Kerlogue, *loc. cit.* | 81—82 | — | 18,000 |
| This paper | 82 and 88 | +92·2 | 19,500 |

The discovery of this new form of $\Delta^4$-cholestenone may be due to the high state of purity in which the ketone was obtained by the chromatographic technique. This is borne out by the somewhat higher rotations and extinction coefficients of the two forms as compared with those previously reported (see table).

Closely related to the phenomena now described is the behaviour of progesterone, the two forms of which were originally believed to be different substances (Slotta, Ruschig, and Blanke, *Ber.*, 1934, **67**, 1947; Butenandt and Schmidt, *ibid.*, p. 2088).

### Experimental.

Chromatogram fractions were crystallised from alcohol before the m. p. was determined. Other conditions were as noted under "Experimental" in Part XLV (preceding paper).

*Chromatographic Analysis of $\Delta^4$-Cholestenone.*—Cholesterol (5 g.) was oxidised as described by Jones, Wilkinson, and Kerlogue (*loc. cit.*); the crude $\Delta^4$-cholestenone (4·3 g.) after one crystallisation had m. p. 78°. Its solution in light petroleum was adsorbed on a 2·9 × 45 cm. column of "Birlec" alumina, and the chromatogram developed with benzene. The following is a typical chromatogram (50 c.c. fractions). (Fractions 2 and 3 were contaminated with resinous substances.)

| Fraction number. | M. p. | M. p. after recrystn. from EtOH. | Fraction number. | M. p. | M. p. after recrystn. from EtOH. |
|---|---|---|---|---|---|
| 2 | 86·5—87·5° | — | 8 | 87·5° | 88° |
| 3 | 87 | — | 9 | 82 | 82 |
| 4 | 87·5 | 88° | 10 | 88 | 88 |
| 5 | 87·5 | 88 | 11 | 82 | 82 |
| 6 | 82 | 82 | 12 | 87·5 | 88 |
| 7 | 88 | 88 | 13 | 88 | 88 |

The various fractions with m. p. 88° were combined and recrystallised without any change in m. p. being observed. The new *form* separated from alcohol in needles (Found: C, 84·6; H, 11·8. $C_{27}H_{44}O$ requires C, 84·3; H, 11·6%); $[\alpha]_D^{20°}$ +92·2° ($c$ = 2·560), +91·9° ($c$ = 1·350). The form with m. p. 82° separated from alcohol in needles, $[\alpha]_D^{20°}$ +92·2° ($c$ = 4·510), +93·6° ($c$ = 3·095). The semicarbazone, prepared from either form, had m. p. 237° (decomp.) (lit., m. p. 237°, decomp.), and the 2 : 4-dinitrophenylhydrazone m. p. 238° (decomp.) (lit., m. p. 238°, decomp.).

Imperial College of Science and Technology, London, S.W. 7. [*Received, July 29th*, 1943.]

---

## 161. *Some Properties of Urea, Biuret, and Triuret.*

By R. Colin Haworth and Frederick G. Mann.

Urea reacts with thionyl chloride to give biuret and triuret, and with sulphuryl chloride and chlorosulphonic acid to give biuret, triuret, or cyanuric acid according to the conditions employed: thiourea does not give similar reactions. The reaction with thionyl chloride affords the best method for the preparation of biuret and triuret, the properties and structure of which are briefly discussed.

Fenton (J., 1882, **41**, 262) has shown that a mixture of urea and metallic sodium when gently heated undergoes a violent reaction, forming sodium cyanamide (unrecorded yield). Moureu (*Bull. Soc. chim.*, 1894, **11**, 1069) claimed that urea when heated with thionyl chloride undergoes dehydration with formation of cyanamide; he isolated the latter as its silver derivative but did not record the yield. Werner * ("Chemistry of Urea," 1923, p. 92) stated that urea is only slowly attacked by thionyl chloride under Moureu's conditions, and gives a yield of cyanamide of only 0·11% of the theoretical. It is noteworthy that Fenton (*loc. cit.*) failed to dehydrate urea with phosphoric oxide, and that Walther (*J. pr. Chem.*, 1909, **79**, 126) found that zinc chloride at 220° converted urea into cyanuric acid.

We have reinvestigated Moureu's work and find that urea when heated with thionyl chloride undergoes solely deamination, and a mixture of biuret and triuret [or carbonyldiurea, $CO(NH{\cdot}CO{\cdot}NH_2)_2$] is thus obtained, the proportion of triuret increasing with that of thionyl chloride employed. No indication of cyanamide formation could be detected. The mixture of biuret and triuret can be readily separated into its pure constituents by crystallisation from water, and this action of thionyl chloride provides the best known method for the preparation of both these compounds. Previous methods for the preparation of triuret, *e.g.*, by the action of carbonyl chloride on urea or oxamide (Schmidt, *J. pr. Chem.*, 1872, **5**, 39, 56; Schiff, *Annalen*, 1896, **291**, 374) or of hydrogen peroxide on uric acid (Schittenhelm and Wiener, *Z. physiol. Chem.*, 1909, **62**, 103; Ohta, *Biochem. Z.*, 1913, **54**, 442; Walters and Wise, *J. Amer. Chem. Soc.*, 1917, **39**, 2476; Venable, *ibid.*, 1918, **40**, 1100), are either troublesome or give only low yields. The formation of biuret by the interaction of urea and thionyl chloride was briefly noted, but without quantitative details, by Warren and Wilson (*Ber.*, 1935, **68**, 957), who considered that Moureu (*loc. cit.*) mistook biuret for cyanamide.

Sulphuryl chloride has, as expected, a more vigorous action than thionyl chloride when heated with urea. By carefully controlling the reaction, however, we have isolated from the reaction product a colourless crystalline *substance* of composition $C_4H_{16}O_7N_6S$. A cold aqueous solution of this substance does not furnish sulphate ions; it is, however, very readily hydrolysed by hot dilute mineral acids to biuret and sulphuric acid. Consequently, it can be extracted from the crude reaction product only if the latter is first neutralised by ammonia or trimethylamine: direct extraction with hot water liberates sufficient acid from traces of unchanged sulphuryl chloride to cause complete hydrolysis, and only biuret then separates when the aqueous

* A paper entitled "The Action of Thionyl Chloride on Urea" by E. A. and A. E. A. Werner (*Sci. Proc. Royal Dublin Soc.*, 1943, **23**, No. 13) has recently been announced, but we have not been able to obtain a copy.

extract is cooled. The constitution of this intermediate compound is unknown. It may be a trihydrate, $C_4H_{10}O_4N_8S,3H_2O$; it is, however, stable indefinitely in a vacuum at room temperature, but when heated at 130°/15 mm. undergoes slow progressive decomposition, and no definite anhydrous derivative could be obtained. No analogous compound could be isolated from the urea–thionyl chloride reaction product.

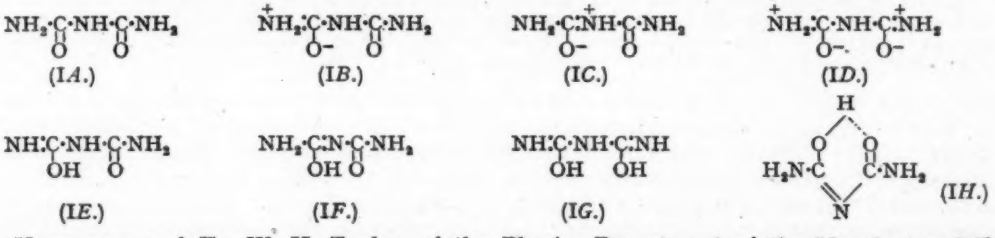
If the interaction of urea and sulphuryl chloride is promoted by direct heating, and the violent reaction then allowed to proceed unchecked, the above compound is not formed, but cyanuric acid is the main product.

Chlorosulphonic acid reacts vigorously with powdered urea even in the cold. When only 0·5 mol. of the acid is used, biuret is again formed, but 1 mol. of the acid gives either cyanuric acid or aminosulphonic acid, $NH_2{\cdot}SO_3H$, with a trace of triuret, according to the conditions employed.

The properties of urea are thus the direct converse of those of thiourea in two important respects. Whereas water cannot normally be abstracted from the urea molecule, hydrogen sulphide can readily be eliminated from thiourea by the action of various metallic oxides, with the consequent formation of cyanamide or (by spontaneous polymerisation) of dicyandiamide. On the other hand, whereas urea readily loses ammonia to give biuret and triuret, no similar reaction occurs with thiourea. We find that boiling thionyl chloride does not react with thiourea; sulphuryl chloride gives only traces of sulphur (being otherwise unchanged); chlorosulphonic acid liberates considerable sulphur, but no other product could be isolated.

Considerable further work is required to elucidate the mechanism by which biuret, triuret, and cyanuric acid are formed by the action of the above acid chlorides on urea. It is clear that the biuret may arise from the hydrolysis of sulphur compounds derived from the acid chlorides used, but there is no definite evidence of the source of the triuret. The cyanuric acid may possibly arise by one or both of two means: (*a*) cyclisation and consequent deamination of triuret, (*b*) polymerisation of cyanic acid formed by direct dissociation of the urea. The likelihood of cyanic acid thus formed reacting with unchanged urea by a "Wöhler rearrangement" to give biuret has been disproved by Davis and Blanchard (*J. Amer. Chem. Soc.*, 1929, **51**, 1806). Biuret undergoes no further deamination when treated with boiling thionyl or sulphonyl chloride.

Certain points concerning the structure of biuret deserve brief discussion, although this structure, like that of urea, must be affected strongly by the environment of the compound. It is clear, however, that biuret may exist as a resonance hybrid between the conventional form (I*A*) and several "zwitterion" forms such as (I*B*), (I*C*), or (I*D*); furthermore, it may exist as partly or fully enolised tautomerides such as (I*E*), (I*F*), or (I*G*). Finally, there is a strong possibility that the structure, particularly in the crystalline state, will be deeply modified by hydrogen bonds, giving cyclic structures, of which one of the simplest is (I*H*) but which may be very much more complex. (The possible structures of triuret are of course far more numerous still.)



(I*A*.) (I*B*.) (I*C*.) (I*D*.)

(I*E*.) (I*F*.) (I*G*.) (I*H*.)

Dr. A. Hargreaves and Dr. W. H. Taylor, of the Physics Department of the Manchester College of Technology, have kindly investigated the structure of crystalline anhydrous biuret; unfortunately this proves to have 8 molecules per unit cell, and this complexity, combined with its space-group, makes elucidation of its molecular structure exceedingly difficult.

Three properties of the biuret structure are noteworthy. (*a*) Some unknown factor in this structure apparently prevents the replacement of both oxygen atoms by sulphur unless other substituents are present to stabilise the molecule. Monothiobiuret, $NH_2{\cdot}CS{\cdot}NH{\cdot}CO{\cdot}NH_2$, and several mono- and di-substituted dithiobiurets, $RNH{\cdot}CS{\cdot}NH{\cdot}CS{\cdot}NH_2$, $RNH{\cdot}CS{\cdot}NH{\cdot}CS{\cdot}NHR$, and $R_1R_2N{\cdot}CS{\cdot}NH{\cdot}CS{\cdot}NH_2$, are known, but the parent dithiobiuret has not been prepared (cf. Wunderlich, *Ber.*, 1886, **19**, 452; Hecht, *Ber.*, 1892, **25**, 749; Fromm *et al.*, *Annalen*, 1893, **275**, 20; 1906, **348**, 161; *Ber.*, 1895, **28**, 1096; 1899, **32**, 835; 1922, **55**, 804).

(*b*) Biuret in alkaline solution usually acts as a dibasic acid, and hence forms a complex bivalent anion with certain heavy metals; *e.g.*, $Na_2[Cu(C_2H_3O_2N_3)_2]$, $Tl_2[Cu(C_2H_2O_2N_3)_2]$, $Ba[Cu(C_2H_3O_2N_3)_2]$, $Tl_2[Ni(C_2H_3O_2N_3)_2]$, and $Ba[Ni(C_2H_3O_2N_3)_2]$ are known, although some of these have water of crystallisation (Schiff, *Annalen*, 1898, **299**, 253; Rising *et al.*, *J. Biol. Chem.*, 1930, **89**, 1; Traube *et al.*, *Ber.*, 1927, **60**, 43; 1930, **63**, 2094; 1935, **68**, 1399).

(*c*) Attention has not previously been directed to the remarkable alternation in properties shown by biuret, triuret, tetrauret, and the next higher homologue, carbonyldibiuret, $CO(NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2)_2$: this alternation appears in the m. p., solubility in cold water, and in ability to give the biuret reaction:

| | M. p. | Solubility in cold water. | Biuret reaction. |
|---|---|---|---|
| $NH(CO{\cdot}NH_2)_2$ | 190° (decomp.) | Moderately soluble | Deep red colour |
| $CO(NH{\cdot}CO{\cdot}NH_2)_2$ | 231 ,, | Slightly soluble | Very faint colour |
| $NH(CO{\cdot}NH{\cdot}CO{\cdot}NH_2)_2$ | 186 ,, | Readily soluble | Intense violet colour |
| $CO(NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2)_2$ | 235 ,, | Almost insoluble | No coloration |

Only qualitative data for solubility in cold water are available. (For general properties of these compounds, see Schmidt, *loc. cit.*; Schiff, *loc. cit.*; Thiele and Uhlfelder, *Annalen*, 1898, **303**, 106.) Our knowledge of the true structure of these compounds is meagre, but it is clear that some unknown factor causes a profound but apparently similar modification in the structure of alternate members.

Since cyanuric acid can be obtained by the action of sulphuryl chloride on urea, a possible route to the preparation of melamine becomes open, because Beilstein (*Annalen*, 1860, **116**, 357) has shown that cyanuric acid is converted by phosphorus pentachloride into cyanuric chloride, and this is readily converted into melamine by heating with ammonia (Hofmann, *Ber.*, 1885, **18**, 2765). Since Beilstein's preparation of cyanuric chloride is both costly and inefficient, we investigated the action of sulphuryl chloride and of chlorosulphonic acid on cyanuric acid, but there was no apparent reaction, for even after several hours' heating treatment with ammonia under Hofmann's conditions gave ammonium cyanurate and not melamine.

The possibility of converting cyanuric acid directly into melamine by the action of ammonia has also been investigated. When the acid was heated in an autoclave with zinc chloride previously saturated with ammonia, ammonium cyanurate was again formed: calcium chloride similarly saturated with ammonia gave calcium cyanurate. These attempts were therefore abandoned.

## Experimental.

*Interaction of Urea and Thionyl Chloride.*—The following are the optimum conditions for the preparation of pure biuret and triuret.

(*a*) *Biuret.* A mixture of dried, finely powdered urea (30 g.) and pure thionyl chloride (13·5 c.c., 0·38 mol.), in a flask having a reflux condenser closed by a calcium chloride tube, was heated on a water-bath for 2·5 hours with occasional vigorous shaking. The flask, whilst still warm, was then evacuated with a water-pump to remove excess chloride, etc. The almost solid product was recrystallised from water (150 c.c.), an undissolved residue of triuret (1 g.; m. p. 225°, efferv.) being collected. The filtrate on cooling deposited monohydrated biuret, which in a vacuum desiccator gave anhydrous biuret, m. p. 186° (efferv.); yield, 14·5 g., 56%. Further recrystallisation from alcohol (*ca.* 400 c.c.) removed a trace of undissolved triuret and gave pure biuret, m. p. 190° (efferv.); yield, 9·7 g., 38% (Found: C, 22·9; H, 4·95; N, 40·5. Calc. for $C_2H_5O_2N_3$: C, 23·3; H, 4·85; N, 40·8%).

(*b*) *Triuret.* A mixture of urea (40 g.) and thionyl chloride (50 c.c., 1 mol.) was treated as in (*a*), and after evacuation the residue was neutralised with a few drops of aqueous ammonia (*d* 0·880) and then recrystallised twice from very dilute aqueous ammonia. Colourless crystals of triuret, m. p. 227° (efferv.), were obtained: 4·8 g., yield 15% (Found: C, 24·6; H, 4·3; N, 38·3. Calc. for $C_3H_6O_3N_4$: C, 24·7; H, 4·1; N, 38·4%). Schiff (*loc. cit.*) gives m. p. 231—232°. The triuret can be obtained by treatment with water alone, but the use of ammonia, by retaining in solution a trace of cyanuric acid, gives a purer product.

*Interaction of Urea and Sulphuryl Chloride.*—(*a*) When dry powdered urea (10 g.) was added to sulphuryl chloride (13·5 c.c., 1 mol.), almost complete dissolution resulted, accompanied by a marked fall in temperature. This solution was heated at 90° for 1 hour, and the excess of chloride then pumped off in a vacuum from the warm product. The crude product, recrystallised from water, furnished biuret (2·6 g.), m. p. 188°, mixed and unmixed.

(*b*) Experiment (*a*) was repeated on a 6-fold scale. The crude product after the vacuum treatment was now, however, neutralised with cold aqueous ammonia (*d* 0·880), and then dissolved by addition of boiling water. The white crystals (9·1 g., m. p. 152° decomp.) obtained on cooling were then recrystallised from 8N-ammonia (300 c.c.). The crystalline product was dried in a vacuum over phosphoric oxide for several days; 6·5 g., m. p. 159° (efferv.) (Found: C, 15·0; H, 4·7; N, 34·8; S, 10·0. $C_4H_{10}O_4N_8S,3H_2O$ requires C, 15·0; H, 5·0; N, 35·0; S, 10·0%). Although this *compound* was thus stable in a vacuum at room temperature, yet when heated at 130°/15 mm. it slowly formed a glassy mass and then an amorphous powder, and its weight fell slowly during many hours: progressive decomposition occurred and it was impossible to prove the presence of water of crystallisation. The function of the ammonia was apparently solely to neutralise sulphuric and hydrochloric acids which would otherwise have been formed during aqueous extraction of the original crude product and would subsequently have caused hydrolysis. The use of aqueous trimethylamine instead of ammonia in this preparation gave ultimately the same product, m. p. 160° (efferv.), unchanged by admixture with the previous sample (Found: C, 15·9; H, 5·2; N, 34·6%).

A cold aqueous solution of this substance gave no immediate precipitate with barium chloride and hydrochloric acid, but on warming, barium sulphate was rapidly precipitated. A mixture of the compound (1 g.) and 1% hydrochloric acid (20 c.c.) was boiled for 10 mins. and was then clear; after 5 mins.' further boiling, the solution was cooled and deposited biuret, 0·2 g., m. p. after dehydration 188—189° (mixed and unmixed) (Found: N, 41·1%).

When the sulphuryl chloride in experiment (*b*) was increased to 6 mols. and the other conditions left unchanged, the same substance was isolated.

(*c*) Experiment (*a*) was repeated, but the original mixture was now heated directly on a sand-bath. Immediately the vigorous initial reaction subsided, the flask was lifted so that it was just not in contact with the sand, and the heating continued for a further 15 mins., an almost solid product being obtained. After the usual evacuation, the product was leached with cold water; the residue (4·4 g.), twice recrystallised from much hot water, gave cyanuric acid, unaffected by heating to 550° (Found: C, 28·0; H, 2·5; N, 32·6. Calc. for $C_3H_3O_3N_3$: C, 27·9; H, 2·3; N, 32·6%).

(*d*) Experiment (*c*) was repeated, but the product after evacuation was treated with excess of aqueous ammonia (*d* 0·880) and then dissolved by addition of boiling water. Cooling gave a white deposit, which when collected and boiled with water evolved ammonia, the solution ultimately depositing cyanuric acid (Found: C, 28·1; H, 2·4; N, 32·9%) on cooling.

(*e*) Experiment (*c*) was repeated, but the reaction mixture was removed from the sand-bath immediately the reaction started. The product became almost solid on cooling, and after the usual evacuation, direct recrystallisation from water gave pure triuret, m. p. 232° (Found: C, 24·8; H, 4·3; N, 38·9%).

*Interaction of Urea and Chlorosulphonic Acid.*—(*a*) When urea (5 g.) and chlorosulphonic acid (2·7 c.c., 0·5 mol.) were mixed, a vigorous reaction ensued and the mixture became semi-solid. The product was heated on a water-bath for 2·5 hours, excess of chlorosulphonic acid removed, and the residue recrystallised from a small quantity of water, giving biuret, m. p. 188° (mixed and unmixed). (*b*) Experiment (*a*) was repeated, but with 1 mol. of chlorosulphonic acid. The residue was mixed with water, set aside for 12 hours, and the undissolved fraction recrystallised from water; aminosulphonic acid, m. p. 207° (mixed and unmixed), was obtained (Found: N, 14·4. Calc. for $H_3O_3NS$: N, 14·4%). The original aqueous extract, taken to dryness and then recrystallised, gave a very small quantity of triuret, m. p. 230° (decomp.), unchanged by admixture with an authentic sample. (*c*) Experiment (*b*) was repeated, the reaction

mixture being heated at 170° for 1 hour. The final residue, recrystallised from much water, gave cyanuric acid, which, when thoroughly dried, was unaffected by heating to 300° (Found: N, 32·4%). Baumgarten (*Ber.*, 1936, **69**, 1929) has shown that urea and sulphuric acid under suitable conditions also give aminosulphonic acid.

Biuret was recovered unchanged after it had been heated (*a*) with thionyl chloride (6 mols.) on a water-bath for 2·5 hours, and (*b*) with sulphuryl chloride (3 mols.) at 90° for 1 hour. When biuret (4 g.) and chlorosulphonic acid (12 c.c., 5 mols.) were mixed in the cold, a vigorous reaction occurred. The mixture, when heated at 100° for 2 hours, became semi-solid. Treatment with cold water gave a crystalline residue of aminosulphonic acid, m. p. 204° (mixed and unmixed), and a further crop was obtained from the aqueous extract. Since no organic compound could be isolated, the biuret had apparently been broken down, carbon dioxide being the main product.

*Reactions of Thiourea.*—Thiourea was also recovered unchanged after it had been heated at 100° for 2·5 hours with (*a*) thionyl chloride (3 mols.), (*b*) sulphuryl chloride (3 mols.); a trace of elementary sulphur was also obtained in the latter experiment. When, however, powdered thiourea (5 g.) and chlorosulphonic acid (4·4 c.c., 1 mol.) were mixed, a vigorous reaction ensued; the mixture, which became yellow, was allowed to cool spontaneously, and after the usual vacuum treatment was extracted with boiling water. Sulphur (1·5 g., representing 70% of that originally in the thiourea) remained, and the filtrate deposited a small quantity of unchanged thiourea. The experiment was repeated but with 3 mols. of chlorosulphonic acid, the mixture being heated on a water-bath for 30 mins. After the usual treatment, extraction with boiling water gave a considerable residue of sulphur; evaporation of the filtrate caused a further minute deposit of sulphur, but no organic residue could be isolated.

*Dicyandiamide from Thiourea.*—A mixture of thiourea (100 g.), powdered litharge (600 g., 2·05 mols.), and hot water (500 c.c.) was boiled under reflux for 3 hours and then rapidly filtered, the residual lead oxide and sulphide being washed on the filter with hot water. The united filtrate and washings were evaporated to *ca.* 120 c.c., and on cooling deposited colourless crystals of dicyandiamide, m. p. 205—206° (mixed and unmixed), 43 g.; a further 3 g. were recovered from the solution. Total yield, 83% of theoretical.

*Molecular Weights of Biuret and Triuret.*—These were determined ebullioscopically. Biuret: *M*, in 0·480% alcoholic solution, 113; in 1·28% solution, 112; in 1·65% solution, 115; in 1·60% aqueous solution, 100; in 3·03% solution, 111; in 4·07% solution, 113; in 5·19% solution, 114 (Calc. for $C_2H_5O_2N_3$: *M*, 103). Triuret: *M*, in 0·55% aqueous solution, 160; in 0·71% solution, 180 (Calc. for $C_3H_6O_3N_4$: *M*, 146). The low solubility of triuret even in boiling water made accurate determinations impossible.

When a solution of triuret (0·50 g.) in boiling water (80 c.c.) was refluxed for 2 hours, no odour of ammonia was detected, and the solution on cooling deposited pure triuret (0·39 g.; m. p. 228°, efferv.): cyclisation to ammonium cyanurate therefore does not occur in these conditions.

Dr. Hargreaves and Dr. Taylor report: "*Biuret.* Rectangular plates have been selected from material recrystallised once from water and twice from alcohol. With light transmitted normally through the plate face and between crossed Nicols straight extinction is observed. An incomplete biaxial optic figure is observed when the crystals are examined in convergent light transmitted normally through the plate face. The density of the crystals, measured by flotation in a mixture of benzene and bromoform, is 1·45$_3$. *X*-Ray rotation and oscillation photographs show that the crystals are monoclinic, with the symmetry axis parallel to the length of the rectangular plates. The *C* face of the crystal being chosen as the plate face, the unit cell dimensions are as follows: $a = 9{\cdot}20$ A., $b = 6{\cdot}6$ A., $c = 15{\cdot}4$ A., $\beta \sim 90°$. With 8 molecules in the unit cell the calculated density is 1·44.

"Indexing of the oscillation photographs indicates that reflections $\{hkl\}$ are present only when $(k + l)$ is even, and $\{h0l\}$ reflections are present only when $h$ is even and $l$ is even. These halvings limit the space-group to either $C_{2h}^5$ or $C_s^4$. The eight molecules in the unit cell lie in completely general positions in lattices with either of these space-groups, and both space-groups are of low symmetry. It would be difficult therefore to proceed any further with the investigation of this compound.

"*Triuret.* The crystals of triuret provided are too small for *X*-ray examination by single crystal methods. Attempts to grow larger crystals have not been successful."

*Reactions of Cyanuric Acid.*—(1) *With sulphuryl chloride.* A mixture of anhydrous cyanuric acid (2 g.) and sulphuryl chloride (5 c.c., 3 mols.) was heated at 90° for 1 hour. The excess of chloride was removed in a vacuum, and the residue boiled with concentrated ammonia solution. The hot clear solution deposited only ammonium cyanurate, which, boiled in hot aqueous solution, ultimately by hydrolysis deposited cyanuric acid (Found: N, 32·1%). No melamine could be detected.

(2) *With chlorosulphonic acid.* A mixture of cyanuric acid (2 g.) and chlorosulphonic acid (6 c.c., 6 mols.) was heated at 160—170° for 2 hours and then treated as in (1). Ammonium cyanurate, giving cyanuric acid (Found: N, 32·4%), was again obtained.

(3) *With zinc chloride–ammonia.* This reagent was prepared by passing dry hydrogen chloride through molten zinc chloride at 280° to remove any basic chloride, then dry hydrogen to remove acid fumes, and finally ammonia, which was passed through for 30 mins. at 280° and then continued as the product cooled. A mixture of this pulverised reagent (40 g.) and cyanuric acid (2 g.) was heated in a sealed tube at 300° for 5 hours. The product on extraction with hot water gave only crude ammonium cyanurate, which afforded cyanuric acid as in (1).

(4) *With calcium chloride–ammonia.* Anhydrous calcium chloride was heated at 160° in a current of hydrogen chloride, which was then replaced by dry air. The salt was then chilled in ice-water, and dry ammonia passed through until absorption ceased. A mixture of this product (27 g.) and anhydrous cyanuric acid (2 g.) was heated in an autoclave at 240° for 8 hours, and when cold was extracted with boiling water (500 c.c.). The solution deposited large crystals, which were recrystallised from water and placed in a vacuum, where they underwent decrepitation and partial dehydration. The residue was apparently calcium cyanurate *tetrahydrate*, but it underwent no further dehydration during 6 hours' exposure to a vacuum at 140° [Found: C, 19·9; H, 3·35; N, 22·7; Ca, 10·7. $(C_3H_3O_3N_3)_2Ca,4H_2O$ requires C, 19·6; H, 3·3; N, 22·8; Ca, 10·9%].

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, September 29th*, 1943.]

---

## 162. *The Preparation and Properties of Certain Poly-sulphanilamide Compounds.*

By FREDERICK G. MANN and JAMES WATSON.

A number of compounds having two, three, or four sulphanilamide groups in the molecule have been prepared and investigated. One compound proved to have slight antibacterial action; otherwise they were therapeutically inactive.

THE vast amount of chemical work on derivatives of sulphanilamide which has followed the discovery of the therapeutic value of the parent compound has been directed mainly in two channels, (*a*) the effect of introducing and interchanging various groups in the sulphanilamide molecule, and (*b*) that of linking the sulphanilamide group to various heterocyclic systems (for a summary of results up to 1940, see Northey, *Chem. Rev.*, 1940, **27**, 85). We have now investigated a third aspect, *viz.*, the effect of introducing several sulphanilamide groups into one molecule, whereby the therapeutic action might be affected both by the number of groups and by their relative spatial position within the molecule. The latter factor is one which has hitherto received comparatively little attention.

It was recognised that any increase in therapeutic action due to the multiplicity of the sulphanilamide groups might be largely counterbalanced by the low solubility of compounds of this type; therefore only poly-sulphanilamido-derivatives of simple aliphatic compounds were prepared, in order to obtain comparatively low molecular weights and hence, it was hoped, reasonably high solubilities. Furthermore, the sulphanilamide units were always linked through the amide groups, in order to leave the *p*-amino-groups unsubstituted, an essential condition for high bactericidal action in the sulphanilamide series.

The condensation of tetrakisaminomethylmethane, $C(CH_2\cdot NH_2)_4$ (Litherland and Mann, J., 1938, 1588), in alkaline solution with *p*-acetamidobenzenesulphonyl chloride could only be effected by working at 45—50° and at great dilution, and by adding sodium hydroxide and the chloride successively in very small quantities; a smooth condensation to give *tetra*-(p-*acetamidobenzenesulphonamidomethyl*)*methane* (I, R = Ac) in high yield then resulted. Hydrolysis with hydrochloric acid gave the required *tetra*-p-*aminobenzene* derivative (I, R = H). Clearly, in this compound the points of attachment of the four sulphanilamido-residues are tetrahedrally arranged around the central carbon atom.

(I.) $C(CH_2\cdot NH\cdot SO_2\cdot C_6H_4\cdot NHR)_4$ $N(CH_2\cdot CH_2\cdot NH\cdot SO_2\cdot C_6H_4\cdot NHR)_3$ (II.)

Similar treatment of ββ′β″-triaminotriethylamine, $N(CH_2\cdot CH_2\cdot NH_2)_3$ (Mann and Pope, *Proc. Roy. Soc.*, 1925, *A*, **109**, 444), gave *tri*-(β-p-*acetamidobenzenesulphonamidoethyl*)*amine* (II, R = Ac) which on acid hydrolysis gave the required *tri*-p-*aminobenzenesulphonamido*-derivative (II, R = H). Although in this molecule the normal oscillations of the three valencies of the central nitrogen atom are possibly affected by the heavy groups to which they are attached, the molecule can be considered as being virtually planar, with the sulphonamidoethyl groups arranged at 120° to one another.

All similar attempts to prepare the corresponding sulphonamido-derivative of γγ′γ″-triaminotripropylamine failed: this amine differs from the ethyl homologue in having a markedly basic tertiary amine group capable of forming stable salts (Mann and Pope, J., 1926, 482, 489) and it was hoped that this property would cause a valuable increase in the water-solubility of the final product.

αα′-Diamino*iso*propyl alcohol (Mann, J., 1927, 2913), when similarly condensed with the sulphonyl chloride and then subjected to acid hydrolysis, gave αα′-*di*-(p-*aminobenzenesulphonamido*)iso*propyl alcohol* (III, R = H): this compound, which was more soluble in water than any other member of the series, has the two sulphonamidomethyl groups held at the tetrahedral angle as in (I). A fourth compound, structurally allied to (III), was obtained from αβγ-triaminopropane, which furnished αβγ-*tri*-(p-*aminobenzenesulphonamido*)*propane* (IV, R = H).

(III.) $CH(OH)(CH_2\cdot NH\cdot SO_2\cdot C_6H_4\cdot NHR)_2$ $NHR\cdot C_6H_4\cdot SO_2\cdot NH\cdot CH(CH_2\cdot NH\cdot SO_2\cdot C_6H_4\cdot NHR)_2$ (IV.)

The fifth compound, differing in general type from the above derivatives, was obtained from *NN′*-di-(β-aminoethyl)ethylenediamine, $C_2H_4(NH\cdot C_2H_4\cdot NH_2)_2$. When this base in pyridine solution was treated with the sulphonyl chloride, NN′-*di*-(p-*acetamidobenzenesulphonyl*)-NN′-*di*-(β-p-*acetamidobenzenesulphonamidoethyl*)-*ethylenediamine* (V, R = Ac) was obtained. This compound on hydrolysis gave the *tetra*-(p-*aminobenzenesulphonamido*)-derivative (V, R = H).

(V.) $[\cdot CH_2\cdot N(SO_2\cdot C_6H_4\cdot NHR)\cdot CH_2\cdot CH_2\cdot NH\cdot SO_2\cdot C_6H_4\cdot NHR]_2$

In spite of the many polar groups in the above *p*-amino-compounds, they all had very low solubilities in water, (III, R = H) being the most soluble. It is significant that Dr. G. Brownlee, of the Wellcome Physiological Research Laboratories, who has investigated these compounds, finds that only the compound (III) has perceptible antibacterial action, and this is too slight to be of value in enteric infections; none of the compounds is apparently absorbed from the gut of the mouse.

Since certain sulphanilamide compounds are known to have an effective action upon monkey malaria, it is always possible that new compounds of this type might prove of value in the treatment of human malaria. Dr. Ann Bishop, of the Molteno Institute of Parasitology, has therefore kindly tested the action of the above polysulphanilamido-compounds upon infections of *Plasmodium relictum* (*a*) transmitted to canaries by intramuscular inoculation of infected blood, and (*b*) induced in canaries by sporozoites. Dr. F. Hawking and Miss I. M. Tonkin, of the National Institute for Medical Research, have also tested the action of compounds (I, III, IV, and V, R = H) on 10-day old chicks which had been infected with *Plasmodium gallinaceum* by intravenous blood injection. None of these compounds, however, showed any antimalarial activity in these tests.

In view of Dr. Brownlee's results with mice, however, it is possible that these compounds are also absorbed only to a negligible extent from the gut of the birds used, and that this factor may have wholly or partly

invalidated the above antimalarial tests, in all of which the compounds were administered orally. Dr. Bishop has therefore further examined compound (III), the most promising of this group, by giving direct intramuscular injections of it to a canary previously infected with *P. relictum* by an intramuscular inoculation of infected blood. Again, no antimalarial action could be detected. In view of these results, it is highly probable that these compounds would also be without effect on human malaria.

## Experimental.

All the sulphonamido-compounds described below were dried for 2 hours at either 80°/15 mm. or 130°/15 mm. (depending on their m. p.'s) before analysis and final m. p. determination: all were colourless when pure. The acid used throughout for hydrolysing the acetamido-compounds was concentrated hydrochloric acid diluted with an equal volume of water.

*Tetra-*(p-*acetamidobenzenesulphonamidomethyl*)*methane* (I, R = Ac).—10% Aqueous sodium hydroxide solution (12·2 c.c., 4 mols.) was added to a suspension of tetrakisaminomethylmethane dihydrogen sulphate (2·5 g.) in water (200 c.c.), and the clear solution of the free base was then warmed to 45—50°. Finely powdered *p*-acetamidobenzenesulphonyl chloride (0·4 g.) and 10% aqueous sodium hydroxide (0·7 c.c.) were then added (the alkali being just sufficient to neutralise the hydrogen chloride liberated by the condensation), and the mixture vigorously shaken for 5 mins. and then reheated to 45—50° for a further 10 mins. Eighteen further similar additions of the chloride and the alkali were then made, followed by the shaking and heating at 45—50° as before, the total addition of the chloride (7·6 g.) being thus 4·3 mols. Excess (25 c.c.) of 10% sodium hydroxide was then added, and the mixture mechanically shaken overnight. The *tetra-acetamido*-compound (I, R = Ac) (3·15 g., 45% of theoretical) which had separated was collected, washed with water and was then pure. A second, less pure fraction was obtained by acidifying the filtrate with hydrochloric acid; the precipitate thus produced was collected, washed with water, dissolved in dilute sodium hydroxide solution, reprecipitated with a slight excess of hydrochloric acid, and finally treated with sodium carbonate solution. This second fraction (1·5 g., 22% of theoretical) was recrystallised from a mixture of glycol monomethyl ether and water. The compound (I, R = Ac) is insoluble in all the usual cold solvents except glycol monomethyl ether: it has m. p. 304—306° (Found: C, 47·9; H, 4·9; N, 11·9. $C_{37}H_{44}O_{12}N_8S_4$ requires C, 48·2; H, 4·8; N, 12·2%).

A mixture of this acetamido-compound (6·3 g.) and dilute hydrochloric acid (250 c.c.), when refluxed for 2 hours, gave a clear pale brown solution. Cooling, followed by addition of excess sodium carbonate, precipitated the crude pale pink *compound* (I, R = H) (5 g., 97%). This product was most satisfactorily purified by warming with water (1 l.), adding 10% sodium hydroxide until a clear solution was obtained, and boiling this with charcoal. The solution was then cooled, filtered, and hydrochloric acid added until the precipitated amino-compound redissolved; the boiling with charcoal was now repeated in the acid solution, which was then again cooled, filtered, and the pure amino-compound (3·4 g.) precipitated by sodium carbonate solution. It is soluble at room temperature only in acetone, and was recrystallised from aqueous acetone; m. p. 243·5—244° (Found: C, 46·5; H, 4·9; N, 14·8. $C_{29}H_{36}O_6N_8S_4$ requires C, 46·2; N, 4·8; N, 14·9%).

*Tri-*(β-p-*acetamidobenzenesulphonamidoethyl*)*amine* (II, R = Ac).—The same method was employed as for the previous acetyl derivative. A solution of ββ′β″-triaminotriethylamine trihydrochloride (2·1 g.) in water (140 c.c.) was decomposed by addition of 10% sodium hydroxide solution (9·8 c.c.), and warmed to 45—50°. Twenty-two successive additions, each of *p*-acetamidobenzenesulphonyl chloride (0·3 g.) and 10% alkali (0·5 c.c.) were then made with vigorous intermediate shaking, and finally 4 further additions of alkali (0·5 c.c.). After 1 hour's final shaking, excess sodium hydroxide was added, and carbon dioxide bubbled through the filtered solution to precipitate the *triacetamido*-compound (5·3 g., 87%). The product, recrystallised from aqueous alcohol (charcoal), softened at 115° and melted at 198·5—200·5° (Found: C, 48·6; H, 6·0; N, 13·3. $C_{30}H_{39}O_9N_7S_3$ requires C, 48·8; H, 5·3; N, 13·3%).

For hydrolysis, a mixture of the triacetamido-compound (4·5 g.) and dilute hydrochloric acid (90 c.c.) was refluxed for 1 hour, a clear solution being readily obtained. This was cooled, diluted with water (150 c.c.), and the crude *tri-p-aminobenzene* derivative (II, R = H) precipitated as a red viscous product by sodium carbonate. It was purified by boiling in hydrochloric acid solution (charcoal), reprecipitation with sodium carbonate, and finally by dissolution in sodium hydroxide solution, followed by precipitation with carbon dioxide. The pure derivative (3·2 g., 86%) separated as a fine powder, which was recrystallised from aqueous acetone; m. p. 178·5—180° (decomp.) (Found: C, 47·5; H, 5·5; N, 16·5. $C_{24}H_{33}O_6N_7S_3$ requires C, 47·15; H, 5·4; N, 16·0%).

All attempts to condense *p*-acetamidobenzenesulphonyl chloride with an aqueous solution of γγ′γ″-triaminotripropylamine failed. Attempted interaction of these compounds in pyridine solution, in boiling ethereal solution in the presence of potassium carbonate, and finally in an acetone solution vigorously agitated with 33% aqueous sodium hydroxide solution, also failed.

αα′-*Di-*(p-*acetamidobenzenesulphonamido*)iso*propyl alcohol* (III, R = Ac).—0·3N-Sodium hydroxide solution was added to a solution of αα′-diamino*iso*propyl alcohol dihydrochloride (1 g.) until the solution was just alkaline to phenolphthalein. The powdered sulphonyl chloride (4·6 g., 3·2 mols.) was added, the mixture warmed to 45—50°, 0·3N-alkali (25 c.c.) added, and the mixture shaken for 15 mins. Successive additions (25 c.c.) of the alkali and shakings at 45—50° were continued until a clear solution was obtained. Cooling, followed by acidification with acetic acid, precipitated the crude *compound* (III, R = Ac) (2·8 g., 95%). This compound is insoluble in most hot liquids, but dissolves in hot nitrobenzene, acetic acid, and the glycol monoalkyl ethers. It was purified by successive extraction with hot water, alcohol, and acetone, followed by crystallisation from aqueous glycol monomethyl ether; m. p. 232·5—233·5° (Found: C, 47·6; H, 5·2; N, 11·4. $C_{19}H_{24}O_7N_4S_2$ requires C, 47·1; H, 5·0; N, 11·6%).

When a mixture of this compound (2·4 g.) and dilute hydrochloric acid (40 c.c.) was refluxed for ¾ hour, and the clear solution then cooled in ice and treated with sodium carbonate, the *di-*(p-*aminobenzenesulphonamido*)-compound (III, R = H) was precipitated, m. p. 177—179°, after recrystallisation from hot water (Found: C, 45·4; H, 5·4; N, 14·0. $C_{15}H_{20}O_5N_4S_2$ requires C, 45·0; H, 5·0; N, 14·0%).

αβγ-*Tri-*(p-*acetamidobenzenesulphonamido*)*propane* (IV, R = Ac).—αβγ-Triaminopropane trihydrochloride monohydrate was prepared by Mann and Pope's method (*Proc. Roy. Soc.*, 1925, *A*, **107**, 80). The highest yield of its tri-*p*-acetamido-derivative was obtained when 21 additions, each of the sulphonyl chloride (0·4 g.) and of 0·5% aqueous sodium hydroxide (13·7 c.c.), were made successively to a solution of the above monohydrate (2·5 g.) in 1% sodium hydroxide (138 c.c.), the product being meanwhile shaken vigorously and kept at 45—50°. Finally, excess of 10% sodium hydroxide solution (*ca.* 50 c.c.) was added, and the shaking continued. A portion of the *tri-*p-*acetamido*-compound (IV, R = Ac) which had not dissolved in the alkali was now collected, and a second crop obtained by treating the filtrate with a small excess of hydrochloric acid and then with much sodium carbonate to redissolve any sulphanilic acid; the two crops when united (5·9 g., 75%) and recrystallised from aqueous acetic acid gave the pure acetamido-compound, m. p. 218·5—220·5° (Found: C, 47·5; H, 5·0; N, 12·4. $C_{27}H_{32}O_9N_6S_3$ requires C, 47·6; H, 4·7; N, 12·35%). The use

of more concentrated alkali in the above preparation, or its replacement by pyridine, caused a marked reduction in the yield of the final product.

For hydrolysis, a mixture of the triacetamido-compound (12 g.) and dilute hydrochloric acid (200 c.c.) was refluxed for 1·5 hours, and the clear brown solution was cooled and treated, first with 30% sodium hydroxide solution until a faint precipitate was obtained, and finally with sodium carbonate solution until precipitation was complete. The *tri*-(p-*aminobenzenesulphonamido*)*propane* (IV, R = H) thus obtained separated at first as a red, and later as a colourless, solid. Purification was best effected by adding the total product to hot water (2 l.), adding 10% sodium hydroxide until complete dissolution was obtained, and then boiling with charcoal for 5 mins. The solution was filtered, treated with hydrochloric acid until a clear solution was again obtained, and the charcoal treatment repeated. Filtration gave a colourless solution, which was cooled and treated cautiously with sodium carbonate solution; the compound (IV, R = H) separated as fine crystals (6·0 g., 62%), which were collected, washed with water, and recrystallised from aqueous acetone; m. p. 234·5—236° (decomp.) with softening at 220° (Found: C, 45·3; H, 4·6; N, 15·3. $C_{21}H_{26}O_6N_6S_3$ requires C, 45·5; H, 4·7; N, 15·2%). This compound is freely soluble in acetone, but almost insoluble in the other common solvents.

*Preparation of* NN′-*Di*-(*β-aminoethyl*)*ethylenediamine*.—Ethylene dibromide (20 c.c.) and ethylenediamine hydrate (54 c.c., 3 mols.) were mixed in a flask fitted with an efficient reflux condenser. After a few minutes, a vigorous reaction ensued with much heat evolution; when this reaction subsided, the mixture was heated at 130—140° for 4 hours. The product was cooled, treated with much powdered potassium hydroxide, and the dried liquid residue distilled first at atmospheric pressure to remove unchanged ethylenediamine and finally at reduced pressure to obtain the above pure tetramine, b. p. 150—152°/16 mm., 158—160°/20 mm.; a high-boiling by-product remained in the distillation flask.

A solution of the above amine (0·62 g.) in dry pyridine (5 c.c.) was added in 1-c.c. portions to a similar solution of the sulphonyl chloride (4·2 g., 4·25 mols.) in pyridine (5 c.c.), the latter being kept vigorously agitated meanwhile. The mixture became warm, developed a dark red colour, and deposited a small quantity of solid. It was then shaken for 2 hours, poured into water (150 c.c.), and the red precipitate of crude *tetra-acetamido*-compound (V, R = Ac) (2·2 g., 55%) collected, washed with water, and recrystallised from aqueous pyridine (charcoal); m. p. 290·5—291·5° (Found: C, 48·0; H, 5·3; N, 11·7. $C_{38}H_{46}O_{12}N_8S_4$ requires C, 48·7; H, 5·0; N, 12·0%). It is freely soluble only in hot pyridine, nitrobenzene, and the lower glycol monoalkyl ethers.

After a mixture of this acetamido-compound (5 g.) and dilute hydrochloric acid (200 c.c.) had been refluxed for 2 hours, some solid still remained undissolved, but a clear solution was obtained by subsequent dilution with hot water (600 c.c.). This solution, when cooled and treated with excess of sodium carbonate, gave the *tetra*-p-*aminobenzenesulphonamido*-compound (V, R = H) (3·4 g., 83%). It was purified by recrystallisation from aqueous glycol monomethyl ether (charcoal), a second crop being obtained by cautious addition of water to the filtrate; m. p. 208—209° (Found: C, 47·4; H, 5·4; N, 14·9. $C_{30}H_{38}O_8N_8S_4$ requires C, 47·0; H, 5·0; N, 14·6%). The compound is freely soluble only in hot nitrobenzene and glycol monomethyl ether.

Dr. Brownlee reports as follows on the compounds (I)—(V), where in all cases R = H:

"In Vitro *Tests*.—*Method A*: where a variable inoculum, diluted serially to the simple powers of 10, is used and the drug concentration is kept constant. The range of organisms included *Streptococcus*, *Staphylococcus*, *B. coli*, *B. typhosus*, *Shiga*, *Flexner* and *Sonne*. Saturated solutions of compounds (I)—(V) in broth have been tested and found inactive except (III), which was effective against all organisms tested except *Staphylococcus*.

*Method B*: where the inoculum is kept constant and the drug concentration is diluted serially to the simple powers of 10. Only the compound (III) was tested: this compound at a dilution of 1 in 2000 in broth inhibited the growth of *Streptococcus*, *B. typhosus*, and *B. dysenteriæ Shiga*.

*Therapeutic Tests*.—Compounds (I)—(V) in doses of 1 mg. and 10 mg. were tested orally for activity against *Streptococci* and *Staphylococci* in groups of six mice. No protection was shown by any compound.

*Tests for absorption from the gut*. Compounds (I)—(V) were fed to mice in doses of 25 mg. per 100 g. of mouse, and the animals bled at hourly intervals for 8 hours. Estimations were made on the blood to determine the drug concentrations, but no drug could be detected in the blood stream. It is concluded that the drugs are not absorbed."

The help received from Dr. G. Brownlee, Dr. A. Bishop, Dr. F. Hawking, and Miss I. M. Tonkin is gratefully acknowledged.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, October 5th*, 1943.]

---

## 163. *Dienoestrol.*

By G. I. HOBDAY and W. F. SHORT.

A second form (m. p. 94—95°) of γδ-bis-4-hydroxyphenylhexane-γδ-diol (I) has been isolated and on dehydration affords *γγ-bis-4-hydroxyphenylhexan-δ-one* (VII), the methyl ether of which is reduced to stilboestrol dimethyl ether (IX). Either *β-chloro*-α-p-*anisyl*-$\Delta^{\alpha}$-*propene* or *α-chloro*-α-p-*anisyl*-$\Delta^{\alpha}$-*propene* can be obtained from anethole dichloride, and the corresponding *bromo*-compounds have been prepared. The α-bromo-compound and magnesium afford *dienoestrol dimethyl ether*, and the β-bromo-compound, to which the α-structure was assigned by Balaban *et al.* (*loc. cit.*), similarly yields αδ-di-*p*-anisyl-βγ-dimethyl-$\Delta^{\alpha\gamma}$-butadiene.

THE important oestrogen dienoestrol, γδ-bis-4-hydroxyphenyl-$\Delta^{\beta\delta}$-hexadiene, (m. p. 227—228°) was prepared by Dodds, Golberg, Lawson, and Robinson (*Nature*, 1938, **142**, 34; *Proc. Roy. Soc.*, 1939, *B*, **137**, 162) from *p*-hydroxypropiophenone by reduction to γδ-bis-4-hydroxyphenylhexane-γδ-diol (I), m. p. 204—206°, followed by dehydration with acetyl chloride and acetic anhydride to γδ-bis-4-acetoxyphenyl-$\Delta^{\beta\delta}$-hexadiene and hydrolysis. Balaban, Jones, and British Colloids (B.P. 547,027) state that dienoestrol, m. p. 192°, may be obtained from the dimethyl ether, m. p. 161°, resulting from the action of magnesium upon a compound, formulated as α-bromo-α-*p*-anisyl-$\Delta^{\alpha}$-propene (II) and obtained by the action of dilute aqueous sodium hydroxide on αβ-dibromo-β-*p*-anisyl*iso*butyric acid. The lower m. p. attributed to dienoestrol by Balaban *et al.* might be due to the fact that they had isolated a different stereoisomer, but the present authors had good theoretical reasons for thinking that the elimination of hydrogen bromide and carbon dioxide from αβ-dibromo-β-*p*-anisyl*iso*butyric acid would produce *β-bromo-α-p-anisyl-*$\Delta^{\alpha}$*-propene* (III), so that the final product of the synthesis would

be αδ-bis-4-hydroxyphenyl-βγ-dimethyl-$\Delta^{\alpha\gamma}$-butadiene (IV). In agreement with this conclusion, ozonolysis of the dimethyl ether, m. p. 163°, gave a 73% yield of anisaldehyde together with diacetyl, and catalytic reduction afforded a compound, m. p. 68—69°, which must be αδ-*di*-p-*anisyl*-βγ-*dimethylbutane* (V), since it is also obtained by the action of magnesium on β-*chloro*-α-p-*anisylpropane*. The bromide (III) is also obtained by the action of alcoholic sodium ethoxide (1·1 mols.) on anethole dibromide and affords β-*p*-anisyl-α-methylacrylic acid, m. p. 158°, by the successive action of magnesium and carbon dioxide. The isomeric bromo-compound (II) has now been prepared by the addition of hydrogen bromide to 1-p-*anisylprop*-1-*yne*, obtained by digesting anethole dichloride successively with pyridine and methyl-alcoholic potash. A small yield of dienoestrol is obtained from this bromide by the successive action of magnesium and anhydrous cupric chloride, followed by demethylation of the product with methylmagnesium iodide.

(I.) $HO\cdot C_6H_4\cdot CEt(OH)\cdot CEt(OH)\cdot C_6H_4\cdot OH$ (II.) $MeO\cdot C_6H_4\cdot CBr{:}CHMe$
(III.) $MeO\cdot C_6H_4\cdot CH{:}CMeBr$ (IV.) $HO\cdot C_6H_4\cdot CH{:}CMe\cdot CMe{:}CH\cdot C_6H_4\cdot OH$
(V.) $MeO\cdot C_6H_4\cdot CH_2\cdot CHMe\cdot CHMe\cdot CH_2\cdot C_6H_4\cdot OMe$ (VI.) $MeO\cdot C_6H_4\cdot CH{:}CMe\cdot NMe\cdot C_6H_5$

Anethole dibromide and boiling dimethylaniline afford β-(N-*methylanilino*)*anethole* (VI) with elimination of methyl bromide, and the unsaturated amine yields anisaldehyde and acetomethylanilide on oxidation. The elimination of hydrogen chloride from anethole dichloride is controlled by the reagent employed. Thus, pyridine produces β-*chloro*-α-p-*anisyl*-$\Delta^{\alpha}$-*propene*, b. p. 135—136°/10 mm., which is also obtained by the action of phosphorus pentachloride on anisylacetone. Ozonolysis affords a 60% yield of anisaldehyde and the successive action of magnesium and carbon dioxide yields β-*p*-anisyl-α-methylacrylic acid, and a small amount of αδ-di-*p*-anisyl-βγ-dimethyl-$\Delta^{\alpha\gamma}$-butadiene. The same formula has been ascribed without proof to the products obtained from anethole and phosphorus pentachloride by Ladenburg (*Annalen, Suppl.*, 1877, **8**, 90) and by the distillation of anethole dichloride (Darzens, *Compt. rend.*, 1897, **124**, 564).

α-*Chloro*-α-p-*anisyl*-$\Delta^{\alpha}$-*propene*, m. p. 43°, is obtained by the action of alcoholic potash on anethole dichloride or from *p*-methoxypropiophenone and phosphorus pentachloride; this isomer resembles α-bromostyrene (Dufraisse, *Compt. rend.*, 1921, **172**, 162) in being readily oxidised in air and we were unable to convert it into dienoestrol dimethyl ether by the action of magnesium.

The pinacol (I) has been obtained from *p*-hydroxypropiophenone and aluminium amalgam in moist ether (Dodds *et al.*, *loc. cit.*) or by electrolytic reduction (Glaxo Laboratories, Robinson, and Resuggan, B.P. 523,515). Its *dimethyl* ether, m. p. 194°, can be obtained from *p*-methoxypropiophenone by reduction electrolytically or with magnesium amalgam and from *p*-anisylmagnesium bromide and dipropionyl, conveniently prepared from propionoin and selenium dioxide. Electrolytic reduction of p-*benzoyloxypropiophenone* results in the simultaneous elimination of the benzoyl group and the main product is an *iso*pinacol, m. p. 94—95°. The *iso*-pinacol, which is probably the racemic form of (I), also accompanies the pinacol when the electrolytic reduction of *p*-hydroxypropiophenone is carried out under different conditions and may be separated by taking advantage of its greater solubility in cold acetic acid. The *iso*pinacol is rapidly converted into γγ-*bis*-4-*hydroxyphenylhexan*-δ-*one* (VII), m. p. 136°, by hot glacial acetic acid or by mineral acids and, although there are indications that the *iso*pinacol affords a dibenzoate, the pure compound could not be isolated owing to the ease with which it is transformed into γγ-*bis*-4-*benzoyloxyphenylhexan*-δ-*one*, m. p. 178°. The keto-phenol (VII) does not react with any of the usual ketonic reagents, but affords a *diacetate*, m. p. 91—92°, and a liquid dimethyl ether (VIII), which yields 4 : 4′-dimethoxybenzophenone on oxidation with chromic anhydride and stilboestrol dimethyl ether (IX), m. p. 124°, on reduction with sodium and amyl alcohol. When the keto-phenol (VII) is fused with potash, it affords αα-bis-4-hydroxyphenylpropane (X), m. p. 134°, which has been synthesised by Wessely, Kerschbaum, Kleedorfer, Prillinger, and Zajic (*Monatsh.*, 1940, **73**, 127). Methylation of the phenol (X) yields αα-di-*p*-anisylpropane, m. p. 44°, which is identical with the product obtained by reducing αα-di-*p*-anisyl-$\Delta^{\alpha}$-propene with sodium and amyl alcohol. The propene was obtained by Gattermann (*Ber.*, 1889, **22**, 1129) as a by-product of a Friedel–Crafts reaction with anisole and propionyl chloride, but the structure assigned to it by him has been disputed by Skraup and Freundlich (*Annalen*, 1923, **431**, 268) on the ground that it depresses the m. p. of an isomeric compound obtained from 4 : 4′-dimethoxybenzophenone and ethylmagnesium bromide, has a yellow colour, and does not exhibit halochromy with concentrated sulphuric acid. We find, however, that Gattermann's compound crystallises from alcohol in colourless plates, m. p. 101°, which give a red coloration with concentrated sulphuric acid.

$$(I) \longrightarrow (HO\cdot C_6H_4)_2CEt\cdot COEt\ (VII.) \longrightarrow (MeO\cdot C_6H_4)_2CEt\cdot COEt\ (VIII.)$$
$$\downarrow \qquad\qquad\qquad\qquad \downarrow$$
$$(HO\cdot C_6H_4)_2CHEt\ (X.) \qquad\qquad MeO\cdot C_6H_4\cdot CEt{:}CEt\cdot C_6H_4\cdot OMe\ (IX.)$$

Dienoestrol is somewhat resistant to methylation, but affords a *mono*- and a *di-methyl* ether, m. p. 142° and 130—131° respectively. These are demethylated to dienoestrol by methylmagnesium iodide, but afford an isomeric *compound*, m. p. 189°, with alcoholic potash at 220°.

(*Note added September* 28th, 1943.) Reduction of the compound, m. p. 189°, obtained by the demethylation of dienoestrol dimethyl ether with alcoholic potash, in presence of palladised charcoal affords a mixture of hexoestrol and *iso*hexoestrol in the ratio 2 : 1. The compound cannot therefore be γδ-bis-4-hydroxyphenyl-$\Delta^{\alpha\epsilon}$-hexadiene. Oxidation of the corresponding dimethyl ether with potassium permanganate in aqueous acetone

gives a small yield of anisil, and ozonolysis affords a trace of anisil and some acetaldehyde (2 : 4-dinitrophenylhydrazone, m. p. 167—168°). The compound is therefore probably a stereoisomeride of dienoestrol and may be called *isodienoestrol*. The liquid dimethyl ether of *iso*dienoestrol affords hexoestrol dimethyl ether, m. p. and mixed m. p. 145°, as main product by reduction in presence of palladised charcoal.

## Experimental.

1-p-*Anisylprop*-1-*yne*.—Crude β-chloro-α-*p*-anisyl-$\Delta^{\alpha}$-propene, b. p. 135—136°/10 mm. (150 g.), potassium hydroxide (135 g.; 2·9 mols.), and methanol (225 c.c.), refluxed for 8 hours, afforded 1-p-*anisylprop*-1-*yne* (90 g. or 75%) as a colourless liquid, b. p. 115—117°/9 mm. (Found: C, 82·3; H, 7·3. $C_{10}H_{10}O$ requires C, 82·2; H, 6·8%).

α-*Chloro*-α-p-*anisyl*-$\Delta^{\alpha}$-*propene*.—(1) Anethole dichloride (257 g.), when refluxed for 4 hours with a solution of sodium (55 g.; 2·8 atoms) in absolute alcohol (1 l.) gave the crude chloride, b. p. 108—110°/6 mm. (115 g. or 53·6%). α-*Chloro*-α-p-*anisyl*-$\Delta^{\alpha}$-*propene*, m. p. 43°, was isolated by freezing (Found: Cl, 19·0. $C_{10}H_{11}OCl$ requires Cl, 19·5%).

(2) Phosphorus pentachloride (55 g.; 1·06 mols.) was added in portions with shaking to *p*-methoxypropiophenone (41 g.) at −5°; after 12 hours, the product was isolated with ether and hydrolysed for 12 hours at room temperature with a solution of potassium hydroxide (14 g.; 1 mol.) in water (14 c.c.) and alcohol (126 c.c.). *p*-Methoxypropiophenone was removed by adding a concentrated aqueous solution of hydroxylamine hydrochloride (7 g.) and potassium hydroxide (11 g.), removing the solvent under diminished pressure, and washing an ethereal solution of the residue with water. The yield of α-chloro-α-*p*-anisyl-$\Delta^{\alpha}$-propene, m. p. 43°, was 20 g. or 44%.

β-*Chloro*-α-p-*anisyl*-$\Delta^{\alpha}$-*propene*.—(1) This *compound*, b. p. 135—136°/10 mm., was obtained in 57% yield by heating anethole dichloride and pyridine (2·3 mols.) on the steam-bath for 2 hours, the operation being repeated with the same amount of pyridine (Found: Cl, 19·4, 19·3. $C_{10}H_{11}OCl$ requires Cl, 19·5%).

(2) A 24% yield of this chloro-compound was also obtained from anisylacetone and phosphorus pentachloride, the same technique being used as that employed in preparing the α-isomer. The structure of the material obtained from anethole dichloride and pyridine was verified (*a*) by the production of anisaldehyde (isolated as 2 : 4-dinitrophenylhydrazone, m. p. 254°) in 60% yield on ozonolysis in chloroform solution with 3% ozonised oxygen and (*b*) by the isolation of β-*p*-anisyl-α-methylacrylic acid, m. p. 158°, and of αδ-di-*p*-anisyl-βγ-dimethyl-$\Delta^{\alpha\gamma}$-butadiene, m. p. 162° (see below), from the products obtained by the successive action of magnesium (5 g.) and of carbon dioxide on a solution of the chloro-compound (25 g.) in anhydrous ether (125 c.c.).

β-(N-*Methylanilino*)*anethole*.—An exothermic reaction occurred when anethole dibromide (308 g.) was mixed with dimethylaniline (250 c.c.; 2 mols.) and, after 24 hours, the mixture was washed with dilute acid and water, to remove dimethylaniline, dried, and distilled. Fraction (1), b. p. 112—113°/7 mm., probably consisted of 1-*p*-anisylprop-1-yne, and fraction (2), b. p. 200—205°/1 mm., solidified on cooling and crystallised from alcohol in colourless leaflets, m. p. 116° (Found: C, 80·8; H, 7·8; N, 5·4. $C_{17}H_{19}ON$ requires C, 80·6; H, 7·5; N, 5·5%). The yield was 100 g. or 39·5% and oxidation with potassium permanganate in acetone solution afforded anisaldehyde (2 : 4-dinitrophenylhydrazone, m. p. 254°) and acetomethylanilide, m. p. 103°.

β-*Bromo*-α-p-*anisyl*-$\Delta^{\alpha}$-*propene* (III).—(1) αβ-Dibromo-β-*p*-anisyl*iso*butyric acid and dilute aqueous sodium hydroxide under the conditions described by Balaban *et al.* (*loc. cit.*) afforded β-*bromo*-α-p-*anisyl*-$\Delta^{\alpha}$-*propene*, b. p. 130—132°/6 mm., in 73% yield (Found: Br, 35·1. $C_{10}H_{11}OBr$ requires Br, 35·25%).

(2) Anethole dibromide and 1·7N-alcoholic potash (1·1 mols.) gave a 40% yield of the same compound when boiled for 3 hours. When the product obtained by either method was converted into a Grignard reagent and carbonated at −10°, it afforded β-*p*-anisyl-α-methylacrylic acid, m. p. 158°, in 25% yield and the structure was further confirmed by conversion of the bromide into αδ-di-*p*-anisyl-βγ-dimethyl-$\Delta^{\alpha\gamma}$-butadiene (see below).

αδ-*Di*-p-*anisyl*-βγ-*dimethyl*-$\Delta^{\alpha\gamma}$-*butadiene* (as IV).—The preceding bromo-compound was brought into reaction with magnesium as described by Balaban *et al.* (*loc. cit.*); the product crystallised from light petroleum–benzene in colourless laminæ, m. p. 163°. Ozonisation of the unsaturated compound (0·1 g.) in chloroform (25 c.c.) with 0·5% ozone for 3 hours at 0°, decomposition of the ozonide with water, and distillation of the liquid furnished a distillate with a strong odour of diacetyl and which afforded nickel dimethylglyoxime after reaction with hydroxylamine. Anisaldehyde (0·06 g. or 73%) was obtained by extracting the residue with ether and was identified by the preparation of its semicarbazone, m. p. 209°, and 2 : 4-dinitrophenylhydrazone, m. p. 254°. [Stilboestrol dimethyl ether, m. p. 124°, afforded *p*-methoxypropiophenone (2 : 4-dinitrophenylhydrazone, m. p. 190—191°) when ozonised under the same conditions.]

αδ-*Di*-p-*anisyl*-βγ-*dimethylbutane* (V).—(i) A solution of the aforesaid unsaturated compound (0·55 g.) in warm acetone (100 c.c.) was shaken with hydrogen in the presence of 6% palladium–charcoal (1 g.), 2·1 mols. of hydrogen being absorbed in 2 hours. The resulting mixture of tetrahydro-compounds (0·49 g.), m. p. 68—75°, on crystallation from alcohol afforded a portion (0·45 g.), m. p. 73—75°, and the mother-liquor deposited crystals, m. p. 67—73°, which on sublimation at 170°/1 mm. and recrystallisation from alcohol furnished αδ-*di*-p-*anisyl*-βγ-*dimethylbutane*, m. p. 68—69° (Found: C, 80·6; H, 8·6. $C_{20}H_{26}O_2$ requires C, 80·5; H, 8·7%). There was a depression in m. p. when this preparation was mixed with αω-di-*p*-anisylhexane, m. p. 70—71°, prepared by the method of Richardson and Reid (*J. Amer. Chem. Soc.*, 1940, **62**, 413). (ii) Reduction of anisylacetone (50 g.) with sodium (50 g.; 7·1 atoms) and absolute alcohol (600 c.c.) gave the secondary alcohol (11 g. or 22%), b. p. 108—109°/2 mm., which afforded β-chloro-α-*p*-anisylpropane, b. p. 89—90°/1 mm., with hydrogen chloride in benzene solution. The yield was 43%, and the chloro-compound gave the butane, m. p. and mixed m. p. 68°, when a dry ethereal solution was boiled with a large excess of magnesium for 4 hours.

γδ-*Bis*-4-*hydroxyphenylhexane*-γδ-*diol* (*Pinacol, m. p.* 204—206°).—This compound, prepared from *p*-hydroxypropiophenone by reduction with aluminium amalgam (Dodds *et al.*, *loc. cit.*) or by electrolytic reduction (Glaxo Laboratories, Robinson, and Resuggan, B.P. 523,515), has been further characterised by the preparation of a *dibenzoate*, m. p. 235—236° (Found: C, 75·1; H, 5·9; Bz, 41·3. $C_{32}H_{30}O_6$ requires C, 75·4; H, 5·9; Bz, 41·2%), and a *ditoluene*-p-*sulphonate*, prisms from benzene, m. p. 205° (Found: C, 62·2; H, 5·5. $C_{32}H_{34}O_8S_2$ requires C, 62·8; H, 5·6%).

γδ-*Di*-p-*anisylhexane*-γδ-*diol*.—The *dimethyl* ether of the preceding pinacol crystallised from ethyl acetate in prisms, m. p. 194° (Found: C, 73·0; H, 7·9. $C_{20}H_{26}O_4$ requires C, 72·7; H, 7·9%), and afforded γγ-di-*p*-anisylhexan-δ-one (see below) as main product when dehydrated by boiling with acetic anhydride–acetyl chloride. It was prepared by three methods: (1) A solution of *p*-methoxypropiophenone (32 g.) and mercuric chloride (11·5 g.) in dry ether (150 c.c.) was added to fine magnesium turnings (10 g.) and dry benzene (100 c.c.), and the mixture boiled for 48 hours. After addition of water (25 c.c.) and 1 hour's boiling, the product was acidified with hydrochloric acid, and the benzene layer washed, dried, and evaporated. Distillation afforded 28 g. of recovered ketone, and crystallisation of the solid residue from benzene–alcohol gave 1 g. of the pure methyl ether. (2) Electrolysis of a solution of *p*-methoxypropiophenone (22 g.) and sodium hydroxide (20 g.) in alcohol (200 c.c.) and water (50 c.c.), the method described in B.P. 523,515 for the reduction of *p*-hydroxypropiophenone being used, afforded 4·9 g. (22%) of γδ-di-*p*-anisylhexane-γδ-diol. (3) A mixture of selenium dioxide (12 g.) and propionoin (20 g.), prepared from ethyl propionate in 52—55% yield by the method of Snell and McElvain (*J. Amer. Chem. Soc.*, 1931, **53**, 750), was slowly distilled; the aqueous distillate, b. p.

90—130°, afforded dipropionyl, b. p. 129—130°, after drying and fractionation. The yield, 7 g. (35·5%), was decreased when the propionoin was diluted with alcohol. A solution of dipropionyl (15 g.) in dry ether (100 c.c.) was slowly added to a Grignard reagent prepared from *p*-bromoanisole (118 g.; 4·7 mols.), magnesium (15·3 g.), and dry ether (500 c.c.); after 3 days, the mixture was refluxed for 2 hours and decomposed with ice-cold hydrochloric acid. After removal of ether and anisole (37 g.) the solid was crystallised from benzene, and 5·75 g. (13%) of γδ-di-*p*-anisylhexane-γδ-diol, m. p. 192—194°, were obtained.

*γδ-Bis-4-hydroxyphenylhexane-γδ-diol* (iso*Pinacol*, *m. p.* 94—95°).—The *iso*pinacol was obtained as by-product when *p*-hydroxypropiophenone was reduced electrolytically as described in B.P. 523,515 and could be separated from the pinacol by taking advantage of its greater solubility in cold acetic acid. On one occasion when a faulty porous pot was used the *iso*pinacol was the main product of the reduction. Benzoylation of *p*-hydroxypropiophenone by the Schotten–Baumann method afforded p-*benzoyloxypropiophenone*, which crystallised from alcohol in needles, m. p. 117° (Found: C, 75·6; H, 5·5. $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·5%). Electrolysis of a solution of the benzoyl derivative (20 g.) and sodium hydroxide (10 g.) in dioxan (200 c.c.) and water (50 c.c.), the apparatus and technique described in the patent mentioned above being used, and rebenzoylation of the product by the Schotten–Baumann method resulted in the production of 10 g. of γγ-bis-4-benzoyloxyphenylhexan-δ-one, m. p. 178°, so that the *iso*pinacol must be the main product of the reduction. The low-melting form of γδ-bis-4-hydroxyphenylhexane-γδ-diol separated from cold acetic acid as a white microcrystalline powder, m. p. 94—95° (Found: C, 71·5; H, 7·1; *M*, cryoscopic in camphor, 309. $C_{18}H_{22}O_4$ requires C, 71·5; H, 7·3%; *M*, 302). The *compound* was very labile and readily underwent pinacolin rearrangement when warmed with acids. Benzoylation by the Schotten–Baumann method produced a product, m. p. 175°, which probably contained the dibenzoate (Found: C, 77·2; H, 5·7. $C_{32}H_{26}O_6$ requires C, 75·4; H, 5·9%. $C_{32}H_{26}O_5$ requires C, 78·0; H, 5·7%), but only γγ-bis-4-benzoyloxyphenylhexan-δ-one (see below) could be obtained by fractional crystallisation and this ketone was readily obtained in pure condition when the crude benzoate was digested with acetic acid for a few minutes.

*γγ-Bis-4-hydroxyphenylhexan-δ-one.*—When the *iso*pinacol was warmed with acid, it afforded *γγ-bis-4-hydroxyphenylhexan-δ-one*, which separated from benzene–light petroleum (b. p. 100°) in prisms, m. p. 136° (Found: C, 76·0; H, 7·1. $C_{18}H_{20}O_3$ requires C, 76·1; H, 7·0%). The *dibenzoate* crystallised from benzene–light petroleum in prismatic needles, m. p. 178° (Found: C, 77·7; H, 5·8. $C_{32}H_{26}O_5$ requires C, 78·0; H, 5·7%), and afforded the phenol when boiled with 10% alcoholic potash. The ketone afforded an acetate, m. p. 91—92°, but did not react with hydroxylamine, semicarbazide or 2 : 4-dinitrophenylhydrazine. Methylation with methyl sulphate and aqueous sodium hydroxide yielded a liquid dimethyl ether, which afforded 4 : 4′-dimethoxybenzophenone, m. p. 143—144° (2 : 4-dinitrophenylhydrazone, m. p. 200—201°), when oxidised with chromic anhydride in acetic acid solution. The dimethyl ether (2 g.) was reduced with sodium (6 g.) in boiling amyl alcohol (40 c.c.) to stilboestrol dimethyl ether (0·05 g.), m. p. and mixed m. p. 124°. When γγ-bis-4-hydroxyphenylhexan-δ-one or its diacetate (1 g.) and potassium hydroxide (2 g.) were maintained at 200° for ½ hour, the neutral product obtained crystallised in prisms, m. p. 134° (Found: C, 78·9; H, 7·0. Calc. for $C_{15}H_{16}O_2$: C, 78·9; H, 7·0%), apparently identical with the αα-bis-4-hydroxyphenylpropane described by Wessely *et al.* (*loc. cit.*). Methylation with methyl sulphate and aqueous sodium hydroxide afforded αα-di-*p*-anisylpropane, m. p. 44°. αα-Di-*p*-anisyl-Δ$^{\alpha}$-propene, prepared as described by Gattermann (*loc. cit.*), had b. p. 180—185°/1 mm. and crystallised from alcohol in colourless plates, m. p. 101°. Reduction of the propene (2 g.) with sodium (2 g.) in boiling amyl alcohol (30 c.c.) afforded unchanged propene (1·1 g.) and a small amount of αα-di-*p*-anisylpropane, m. p. and mixed m. p. 44°.

*Dienoestrol.*—The reaction between 1-*p*-anisylprop-1-yne and a 32% (w./v.) solution of hydrogen bromide in acetic acid was exothermic; the temperature rose rapidly if the mixture were not cooled and decomposition occurred. Dry hydrogen bromide (16·5 g.; 1 mol.) was passed into an ice-cold solution of the propyne (30 g.) in benzene (100 c.c.) and, after 2 hours at 0°, 20 c.c. of the solvent were removed in a vacuum at 20°; hardly any hydrogen bromide was liberated. Half the residual solution was added to magnesium turnings (2·5 g.; 0·5 atom) and ether (100 c.c.) and, when the brisk reaction had subsided, the mixture was boiled for an hour; after the addition of another 2·5 g. of magnesium and the rest of the benzene solution, the mixture was refluxed for a further 2 hours, and anhydrous cupric chloride (28 g.; 1 mol.) then added. When the vigorous reaction abated, the mixture was boiled for 12 hours, and the product worked up in the usual way. Distillation afforded (i) anethole (9 g.), b. p. 80—85°/1·5 mm., (ii) 3 g., b. p. 104—105°/1·5 mm., probably the propyne, and (iii) a resinous residue (14 g.). The last was dissolved in ether and evaporated with a solution of methylmagnesium iodide (from magnesium, 3·1 g., methyl iodide, 19 g., and ether, 150 c.c.). When the residue was heated to 170°, there was a vigorous reaction with some carbonisation. The product was decomposed with ice-cold dilute hydrochloric acid, and a solution of the alkali-soluble portion of the product precipitated with carbon dioxide. The precipitate, sublimed at 130°/1 mm., afforded dienoestrol (0·05 g.), m. p. and mixed m. p. 230—233°.

When dienoestrol (5 g.) and an ethereal solution of diazomethane (140 c.c.; 2·2 mols.) were kept at room temperature for 4 days, 3·5 g. of dienoestrol were recovered and 0·7 g. of *dienoestrol monomethyl ether* obtained. This was soluble in alcoholic alkali and separated from aqueous alcohol in needles, m. p. 142° (Found: C, 81·0; H, 7·2; OMe 11·1. $C_{19}H_{20}O_2$ requires C, 81·4; H, 7·1; OMe, 11·1%). Methylation of dienoestrol in N-sodium hydroxide (4·3 mols.) with methyl sulphate (4·0 mols.) afforded the monomethyl ether in 73% yield together with the *dimethyl* ether, m. p. 130—131° (Found: C, 81·4; H, 7·5; OMe, 21·4, 21·5. $C_{20}H_{22}O_2$ requires C, 81·6; H, 7·5; OMe, 21·1%). The mono- and the di-methyl ether were obtained in 29 and 30% yield respectively when dienoestrol, methyl iodide (3·6 mols.), and 0·2N-methyl-alcoholic potash (1·2 mols.) were boiled for an hour. Ozonolysis of dienoestrol dimethyl ether in glacial acetic acid solution afforded a 16% yield of anisil, m. p. 133°, characterised by conversion into 2 : 3-*di*-p-*anisylquinoxaline*, m. p. and mixed m. p. 149—150° (Found: C, 77·2; H, 5·4; N, 7·8. $C_{22}H_{18}O_2N_2$ requires C, 77·2; H, 5·3; N, 8·2%). *Dienoestrol dibenzyl ether* separated from benzene in prisms, m. p. 205° (Found: C, 85·4; H, 6·5. $C_{32}H_{30}O_2$ requires C, 85·9; H, 6·8%). *Dienoestrol ditoluene-p-sulphonate* had m. p. 168° (Found: C, 66·2; H, 5·1. $C_{32}H_{30}O_6S_2$ requires C, 66·8; H, 5·2%). *Dienoestrol dibenzoate* separated from benzene–light petroleum in needles, m. p. 224° (Found: C, 80·3; H, 5·3. $C_{32}H_{26}O_4$ requires C, 81·0; H, 5·3%).

Demethylation of dienoestrol dimethyl ether with methylmagnesium iodide (2·5 mols.) at 175° regenerated dienoestrol, but demethylation with alcoholic potash at 220° afforded an isomeric *compound*, m. p. 189° (Found: C, 81·1; H, 6·8. $C_{18}H_{18}O_2$ requires C, 81·2; H, 6·7%), which afforded a liquid methyl ether.

RESEARCH LABORATORIES, MESSRS. BOOTS PURE DRUG CO., LTD., NOTTINGHAM. [*Received, August 24th*, 1943.]

# 164. β-Cholesterol Oxide.

By R. A. Baxter and F. S. Spring.

As suggested by Hattori (*J. Pharm. Soc. Japan*, 1940, **60**, 334), the β-cholesterol oxide described by numerous investigators is a mixed crystal of α-cholesterol oxide and a new β-cholesterol oxide. Fission of α-cholesterol oxide and its derivatives with hydrochloric acid gives solely chlorohydrins of type (I); similar fission of β-cholesterol oxide derivatives gives only chlorohydrins of type (II).

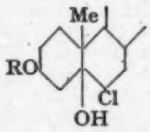
Hydrolysis of the β-cholesteryl benzoate oxide, m. p. 151—152° (Spring and Swain, J., 1939, 1356) gives as major product the β-cholesterol oxide, m. p. 107—108°, $[\alpha]_D^{21°}$ − 15°, described by several investigators (Westphalen, *Ber.*, 1915, **48**, 1064; Windaus, *Z. physiol. Chem.*, 1921, **117**, 146; Ruzicka and Bosshard, *Helv. Chim. Acta*, 1937, **20**, 244). From the mother-liquors of the compound, m. p. 107—108°, we have isolated an oxide, m. p. 131—132°, $[\alpha]_D^{18·5°}$ + 11·5, which has been further characterised by the preparation of its acetate, m. p. 111°, and *benzoate*, m. p. 172—173°. A comparison of the specific rotations of the three oxides suggests that the original β-oxide is in reality a 1 : 1-mixed crystal of α-cholesterol oxide and the new oxide; a similar relationship exists for the three acetate oxides. The specific rotations, $[\alpha]_D$, recorded below were measured in chloroform solution at temperatures between 18° and 23°:

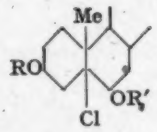
| | α. | αβ (previously β). | β. |
|---|---|---|---|
| Cholesterol oxide | −43·3° | −15·0° | +11·5° |
| Cholesteryl acetate oxide | −43·8 | −21·1 | ± 0 |
| Cholesteryl benzoate oxide | −31·3 | + 3·6 | +16 |

This relationship has been confirmed by the artificial preparation of a mixed crystal by the crystallisation of a mixture of equal parts of α-cholesterol oxide and the new oxide from methanol. This mixed crystal, m. p. 107—108°, $[\alpha]_D$ − 15·4°, is indistinguishable from the original β-cholesterol oxide; the latter is designated αβ-cholesterol oxide and the new compound, β-cholesterol oxide. The optical rotations indicate that the previously described β-cholesteryl benzoate oxide is a 1 : 2-mixed crystal of the α-benzoate oxide and the new β-benzoate oxide. This relationship explains the isolation of β-cholesterol oxide in addition to αβ-cholesterol oxide when the benzoate mixed crystal is hydrolysed.

Hattori (*J. Pharm. Soc. Japan*, 1940, **60**, 334; *Chem. Abs.*, 1940, **34**, 7294) has described a β-cholesterol oxide, m. p. 136°, $[\alpha]_D$ − 10·4°; this compound was obtained by treatment of 5-chloro-3 : 6-diacetoxycholestane with alcoholic potassium hydroxide. We have repeated the experiment and obtained β-cholesterol oxide, m. p. 131—132°, $[\alpha]_D$ + 10·7°,* identical with the new oxide described above.

Treatment of α-cholesterol oxide and its benzoate with benzoyl chloride and pyridine, or of the α-benzoate oxide with hydrochloric acid gives 6-chloro-5-hydroxy-3-benzoyloxycholestane (I, R = COPh) (Spring and Swain, *loc cit.*). Subsequently, similar fissions of the α-oxide and its derivatives have been described, in each case leading to chlorohydrins of type (I) (Hattori, *loc. cit.*; Chakravorty and Levin, *J. Amer. Chem. Soc.*, 1942, **64**, 2317). The fission of αβ-cholesterol oxide and its derivatives, however, presents a more complicated picture. Ruzicka and Bosshard (*loc. cit.*) obtained (I, R = COMe) by treatment of the αβ-acetate oxide with hydrogen chloride. Spring and Swain (*loc. cit.*) observed the opposite type of fission when the αβ-oxide or its benzoate

(I.) 

(II.)

was treated with benzoyl chloride and pyridine, the product being (II, R = R′ = COPh), and also when the αβ-benzoate oxide was treated with hydrochloric acid, the product in this case being (II; R = COPh, R′ = H). Hattori (*loc. cit.*) observed both types of fission when αβ-cholesteryl acetate oxide was treated with hydrogen chloride, the chlorohydrin (II; R = COMe, R′ = H) being isolated in addition to (I, R = COMe). Finally, Chakravorty and Levin (*loc. cit.*) report that treatment of the αβ-oxide and of the αβ-acetate oxide with benzoyl chloride and pyridine gives (I, R = COPh) and (I, R = COMe) respectively; no chlorohydrin of type (II) was observed among their products. In view of this apparent confusion, we have examined the fission of both αβ-cholesterol oxide and its derivatives and that of the new β-cholesterol oxide and its derivatives.

As reported by Spring and Swain, we find that the αβ-oxide (20%) and the αβ-benzoate oxide (55%) both give the dibenzoate (II, R = R′ = COPh) when treated with benzoyl chloride and pyridine. In the former case, a second substance is formed which is probably (I, R = COPh). Again, in contrast to the observation of Chakravorty and Levin (*loc. cit.*), we find that treatment of αβ-cholesteryl acetate oxide with the same reagent gives *5-chloro-3-acetoxy-6-benzoyloxycholestane* (II; R = COMe, R′ = COPh), m. p. 176°, as major isolable product together with a small quantity of 6-chloro-5-hydroxy-3-acetoxycholestane (I, R = COMe). The dual nature of the fission of αβ-cholesterol oxide derivatives was further confirmed in the case of the acetate, which, when treated with hydrogen chloride, gave 5-chloro-6-hydroxy-3-acetoxycholestane (II; R = COMe,

* We have not had access to the original paper of Hattori; the sign of the rotation for the oxide quoted in the abstract may be a misprint.

R′ = H) in addition to the chlorohydrin (I, R = COMe) previously obtained by Ruzicka and Bosshard (compare Hattori, *loc. cit.*). Similar treatment of αβ-cholesterol oxide gives 5-chloro-3 : 6-dihydroxycholestane (II, R = R′ = H).

In agreement with the experiments of Hattori, we find that fission of derivatives of the β-oxide is simple, giving only chlorohydrins of type (II) in yields approximating to 90%. Thus with benzoyl chloride and pyridine the β-benzoate oxide gives the dibenzoate (II, R = R′ = COPh), similar treatment of the β-acetate oxide gives (II; R = COMe, R′ = COPh), and the β-acetate oxide with hydrogen chloride gives 5-chloro-6-hydroxy-3-acetoxycholestane (II; R = COMe, R′ = H). In all the cases examined, fission of αβ-cholesterol oxide derivatives gives chlorohydrins of type (II), the formation of which is to be attributed to the β-cholesterol oxide content of the original oxide. In some cases—where solubility relationships have been favourable—we have in addition obtained chlorohydrin derivatives of type (I), the formation of which is to be attributed to the α-cholesterol oxide content of the original oxide.

## Experimental.

Specific rotations are measured in chloroform in a 1 dm. tube.

*α- and αβ-Cholesteryl Benzoate Oxides.*—Spring and Swain (*loc. cit.*) used perbenzoic acid for the preparation of these oxides. Whereas Chakravorty and Levin (*loc. cit.*) report that oxidation of cholesteryl benzoate with monoperphthalic acid gives only the α-benzoate oxide, we find that this reagent yields the same mixture of oxides as perbenzoic acid. The conditions employed were those described by the latter authors. The chloroform-soluble reaction product from cholesteryl benzoate (16·7 g.) was dissolved in boiling ethyl acetate (*ca.* 500 c.c.). The first crop of prismatic needles (9·5 g.; 56%) consisted of the α-benzoate oxide, m. p. 167—168°, which after one recrystallisation attained the constant m. p. 168—169°. Concentration of the original mother-liquor to 150 c.c. gave αβ-cholesteryl benzoate oxide, m. p. 150—151°, $[\alpha]_D^{20°}$ + 3·6° (*c* = 1·4) (after one recrystallisation from ethyl acetate). By combining and concentrating mother-liquors, a total yield of 5·5 g. (32%) of the αβ-benzoate oxide was obtained. It was identical with the " β-cholesteryl benzoate oxide " of Spring and Swain.

*β-Cholesterol Oxide.*—(*a*) Hydrolysis of αβ-cholesteryl benzoate oxide (20 g.) as described by Spring and Swain (*loc. cit.*), followed by crystallisation of the product from methyl alcohol, gave a top crop of αβ-cholesterol oxide, which after four crystallisations from the same solvent formed needles, m. p. 107—108°, $[\alpha]_D^{20°}$ − 15° (*c* = 1·1). Acetylation gave αβ-cholesteryl acetate oxide as plates from methyl alcohol, m. p. 111—112°, $[\alpha]_D^{19°}$ − 21·1° (*c* = 1·6) (Chakravorty and Levin give $[\alpha]_D$ −12·7° for the αβ-oxide and −21·8° for the αβ-acetate oxide prepared from cholesteryl acetate).* The original methyl-alcoholic mother-liquor of the αβ-oxide deposited a crop of fine needles, which after two crystallisations from the same solvent gave β-cholesterol oxide (2 g.), m. p. 131—132°, $[\alpha]_D^{18·5°}$ + 11·5° (*c* = 1·4) (Found: C, 80·1; H, 11·3. Calc. for $C_{27}H_{46}O_2$: C, 80·6; H, 11·45%). The acetate separated from methanol in fine needles, m. p. 111°, $[\alpha]_D^{18°}$ ± 0° (*c* = 1·5) (Found: C, 78·1; H, 10·8. Calc. for $C_{29}H_{48}O_3$: C, 78·3; H, 10·8%). The *benzoate*, prepared by means of benzoic anhydride and pyridine, separated from methanol in plates, m. p. 172—173°, $[\alpha]_D^{22°}$ + 16° (*c* = 0·9)( Found: C, 80·7; H, 9·8. $C_{34}H_{50}O_3$ requires C, 80·6; H, 9·9%).

(*b*) 5-Chloro-3 : 6-diacetoxycholestane (m. p. 112—113°, 3 g.) was refluxed with alcoholic potassium hydroxide (10%; 60 c.c.) for 2 hours. The solution was diluted with water, and the product isolated by means of ether and crystallised from methanol, yielding β-cholesterol oxide (1·5 g.) in needles, m. p. 131—132°, $[\alpha]_D^{18·5°}$ + 10·7° (*c* = 1·4) (Found: C, 80·2; H, 11·3%). The m. p. of a mixture with the β-oxide described under (*a*) was undepressed. The acetate separated from methanol in long needles, m. p. 111° either alone or when mixed with the acetate described under (*a*); $[\alpha]_D^{21°}$ ± 0° (*c* = 1·5) (Found: C, 78·3; H, 11·0%).

*Oxide Fissions.*—(A) *With benzoyl chloride and pyridine.* (a) The αβ-oxide (5 g.) in pyridine (20 c.c.) and benzoyl chloride (16 c.c.) was heated on the steam-bath for 2 hours. The product, isolated in the usual manner, was crystallised twice from ethyl acetate–methyl alcohol and twice from ethyl acetate to give 5-chloro-3 : 6-dibenzoyloxycholestane (1·0 g.) in hard prisms, m. p. 183—184°, undepressed by an authentic specimen, $[\alpha]_D^{21°}$ −68·8° (*c* = 1·8) (Found: C, 75·8; H. 8·4. Calc. for $C_{41}H_{55}O_4Cl$: C, 76·05; H, 8·6%). The original mother-liquor gave a material which after six crystallisations from methyl alcohol formed needles, m. p. 193—194° (not constant); this was probably impure 6-chloro-5-hydroxy-3-benzoyloxycholestane (Spring and Swain. *loc. cit.*, give m. p. 202—203°); the m. p. of a mixture with the latter was not depressed. *

(b) Similar treatment of αβ-cholesteryl benzoate oxide (2·0 g.) gave 5-chloro-3 : 6-dibenzoyloxycholestane (1·1 g.) in hard prisms from ethyl acetate, m. p. 183—184°, $[\alpha]_D^{20°}$ − 67·9° (*c* = 1·55), undepressed in m. p. when mixed with an authentic specimen.

(c) Similar treatment of β-cholesteryl benzoate oxide (m. p. 172—173°, 0·2 g.) gave 5-chloro-3 : 6-dibenzoyloxycholestane (0·18 g.), m. p. 183—184° either alone or mixed with an authentic specimen; $[\alpha]_D^{21°}$ − 68·2° (*c* = 1·2).

(d) Similar treatment of αβ-cholesteryl acetate oxide (2 g.), followed by crystallisation of the product from ethyl acetate–methanol, gave a first crop, which was twice recrystallised from the same solvent to give *5-chloro-3-acetoxy-6-benzoyloxycholestane* (0·5 g.) in needles, $[\alpha]_D^{22°}$ − 75·8° (*c* = 0·7), m. p. 176°, depressed to 150—160° by 6-chloro-5-hydroxy-3-acetoxycholestane (Found: C, 74·0; H, 9·0. $C_{36}H_{53}O_4Cl$ requires C, 73·9; H, 9·1%). The mother-liquor of the first crop was evaporated, and the residue thrice crystallised from methyl alcohol to give felted needles of 6-chloro-5-hydroxy-3-acetoxycholestane (0·1 g.), $[\alpha]_D^{18°}$ − 27° (*c* = 1·0), m. p. 186—187°, undepressed by the specimen prepared as described below.

(e) Similar treatment of β-cholesteryl acetate oxide (0·3 g.) gave 5-chloro-3-acetoxy-6-benzoyloxycholestane (0·28 g.), $[\alpha]_D^{23°}$ − 74·0° (*c* = 1·3), m. p. 176°, undepressed by the specimen described at (d).

(B) *With hydrogen chloride in chloroform.* (a) αβ-Cholesterol oxide (2 g.) in chloroform (100 c.c.) was treated with a stream of dry hydrogen chloride for 30 minutes. After 24 hours the separated solid was collected (1·0 g; m. p. 155—160°) and crystallised first from ethyl acetate–methanol and then from light petroleum (b. p. 60—80°), from which 5-chloro-3 : 6-dihydroxycholestane separated in needles, m. p. 171°, $[\alpha]_D^{19°}$ − 22·5° (*c* = 1·0) (Found: C, 73·9; H, 10·7. Calc. for $C_{27}H_{47}O_2Cl$: C, 73·8; H, 10·7%). Acetylation gave the corresponding diacetate, which separated from methanol in needles, m. p. 112—113° (Found: C, 71·3; H, 9·8. Calc. for $C_{31}H_{51}O_4Cl$: C, 71·15; H, 9·8%).

(b) αβ-Cholesteryl acetate oxide (2 g.) was similarly treated in pure dry chloroform (15 c.c.) solution with dry hydrogen chloride for 30 minutes. After standing overnight, the solvent was removed, and the residue fractionally crystallised from ethyl acetate–methyl alcohol. The first crop formed felted needles which after two recrystallisations from the same solvent gave 6-chloro-5-hydroxy-3-acetoxycholestane in felted needles (0·7 g.), m. p. 186—187°, $[\alpha]_D^{18°}$ − 26·7° (*c* = 1·1)

* The solvent in which these measurements were made is not recorded.

(Found : C, 72·4; H, 10·15. Calc. for $C_{29}H_{49}O_3Cl$ : C, 72·4; H, 10·2%) [Ruzicka and Bosshard, *loc. cit.*, give m. p. 191° (corr.) for this compound but do not record a specific rotation]. The second crop formed plates, which after two crystallisations from ethyl acetate–methyl alcohol gave 5-chloro-6-hydroxy-3-acetoxycholestane (0·15 g.), m. p. 190—191° (Found : C, 72·0; H, 10·4. Calc. for $C_{29}H_{49}O_3Cl$ : C, 72·4; H. 10·4%). The m. p. was not altered by repeated crystallisations from this solvent; Hattori (*loc. cit.*) gives m. p. 198—200° for this substance. When benzoylated, it gave 5-chloro-3-acetoxy-6-benzoyloxycholestane as needles from ethyl acetate–methanol, $[\alpha]_D^{15\cdot5°}$ — 73·0° ($c$ = 0·5), m. p. 176°, undepressed by the specimen described at A(d).

(c) Fission of β-cholesteryl acetate oxide (1·0 g.) as described at (a) gave 5-chloro-6-hydroxy-3-acetoxycholestane (0·8 g.) as plates from ethyl acetate–methyl alcohol, $[\alpha]_D^{22°}$ — 24·3° ($c$ = 1·3), m. p. 190—191°, undepressed by the specimen prepared by method (a).

(C) *With alcoholic hydrochloric acid.* (a) αβ-Cholesterol oxide (2 g.) in absolute methylated spirit (60 c.c.) containing hydrochloric acid (*d* 1·16; 4 c.c.) was refluxed for 30 minutes. Water was added until the solution was turbid and the solid separating on cooling was crystallised from ethyl acetate–methanol. Recrystallisation from light petroleum (b. p. 60—80°) gave the 5-chloro-3 : 6-diol (0·5 g.) in needles, m. p. 170—171°, $[\alpha]_D^{19°}$ — 22·1° ($c$ = 1·2). The diacetate formed needles, m. p. 112—113° either alone or when mixed with the diacetate prepared by method B(a).

(b) Similar treatment of αβ-cholesteryl acetate oxide (2 g.) gave the 5-chloro-3 : 6-diol (0·4 g.) in needles, m. p. 170—171°, $[\alpha]_D^{20°}$ — 21·5° ($c$ = 1·4) (Found : C, 73·9; H, 10·4. Calc. for $C_{27}H_{47}O_2Cl$ : C, 73·8; H, 10·7%). The dibenzoate formed hard prisms from ethyl acetate, m. p. 184°, undepressed by an authentic specimen. The three specimens of the 5-chloro-3 : 6-diol prepared by methods B(a), C(a) and C(b) showed no depression in m. p. when mixed with each other or with a specimen prepared by the method of Windaus (*loc. cit.*).

THE UNIVERSITY, MANCHESTER.

[*Received, August 27th*, 1943].

---

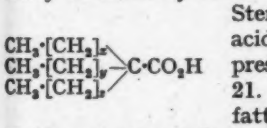
## 165. *Long-chain Acids containing a Quaternary Carbon Atom. Part II.*

By N. POLGAR and SIR ROBERT ROBINSON.

The provisional formulation of phthioic acid as ethyl-*n*-decyl-*n*-dodecylacetic acid (Stenhagen and Ställberg, *J. Biol. Chem.*, 1941, **139**, 345) has been proved incorrect by the synthesis of the substance. For this purpose the method of Hudson and Hauser (*J. Amer. Chem. Soc.*, 1940, **62**, 2457; 1941, **63**, 3156) has been employed. A discussion of the present state of the problem is included and our conclusion, in which we believe Dr. Stenhagen concurs, is that the chain must be longer than thought possible heretofore on the *X*-ray evidence. It seems that any structure with two long chains of comparable length will be found inconsistent with the small area of the compressed films of phthioic acid. Hence there is probably only one long chain and the smaller apparent length is due to considerable tilting of the molecules.

THE present investigation was undertaken in connexion with the study of the structure of phthioic acid, $C_{26}H_{52}O_2$, which was isolated from the lipoid fraction of tubercle bacilli by Anderson and his associates (*Physiol. Rev.*, 1932, **12**, 166; *J. Biol. Chem.*, 1936, **112**, 759; and other papers) and has aroused considerable interest because of its ability to produce lesions similar to those characteristic of tuberculosis.

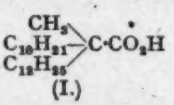
Methods of chemical degradation have thrown little clear light on the structure of phthioic acid, but from a study of monolayers on water and from examination of barium phthioate multilayers by *X*-ray reflection, Stenhagen and Ställberg (*loc. cit.*) concluded that phthioic acid is a trisubstituted acetic acid with one short hydrocarbon chain and two long chains of unequal length as expressed by the annexed formula, where $x$ and $y$ are 8—13, $z$ = 0 or 1, and $x + y + z$ = 21. These authors suggested that the concept of phthioic as a methylated long-chain fatty acid, which was derived by Spielman and Anderson (*J. Biol. Chem.*, 1936, **112**, 759), partly by analogy with tuberculostearic acid, did not appear compatible with the physical evidence.



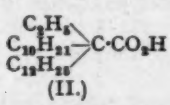
Recently, Schneider and Spielman (*J. Biol. Chem.*, 1942, **142**, 345) have expressed the view that the chemical evidence is consistent with the above formula except for the isolation, by Anderson and Spielman, of an oxidation product, a steam-volatile $C_{11}$-acid, not identical with undecoic acid. Furthermore, azelaic acid was found by Wagner-Jauregg (*Z. physiol. Chem.*, 1937, **247**, 135) among the oxidation products of phthioic acid. Schneider and Spielman point out, however, that these facts can be accommodated if the above formula is modified so that at least one of the long chains is methylated or otherwise branched.

In Part I (Birch and Robinson, J., 1942, 488) a survey was made of the methods applicable to the synthesis of long-chain acids containing a quaternary carbon atom. We have now obtained further trisubstituted acetic acids by use of the valuable method of Hudson and Hauser (*loc. cit.*), which depends on the α-alkylation of esters with sodium triphenylmethyl and alkyl halides in ethereal solution.

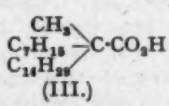
For the preparation of *methyl*-n-*decyl*-n-*dodecylacetic acid* (I) and *ethyl*-n-*decyl*-n-*dodecylacetic acid* (II), methyl *n*-decyl-*n*-dodecylacetate was employed, and its sodium-enolate brought into reaction with methyl iodide and ethyl iodide respectively. *Methyl*-n-*heptyl*-n-*tetradecylacetic acid* (III) and *methyldi*-n-*heptylacetic acid* (IV) were obtained in the same way from *methyl* n-*heptyl*-n-*tetradecylacetate* and methyl di-*n*-heptylacetate by interaction with sodium triphenylmethyl and methyl iodide.



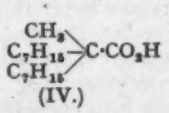
(I.)



(II.)



(III.)



(IV.)

In all cases sodium triphenylmethyl was used in excess and the average yields of the product were 70—80% if the ester was allowed to react with sodium triphenylmethyl for about 3—4 hours. This yield was considerably

decreased when the reaction mixture was kept overnight, presumably as the result of self-condensation of the ester. Still smaller yields were obtained by repetition of the processes.

It was found that the trisubstituted acetic acids obtained on hydrolysis of the products contained unchanged disubstituted acetic acids and full purification was tedious and difficult. Except in the case of ethyldecyldodecylacetic acid, which is discussed later, all attempts to remove the disubstituted acid by partial esterification, by partial hydrolysis of the esters, by conversion into lead salts, or by renewed treatment of the ester with sodium triphenylmethyl and alkyl iodide proved unsuccessful. Finally, the pure acids were obtained by fractional crystallisation of their amides. The trisubstituted acetamides were much more readily soluble than the disubstituted acetamides and had lower melting points; *e.g.*, *methyldecyldodecylacetamide* has m. p. 42° and decyldodecylacetamide has m. p. 112·5°. The pure amides readily furnished the corresponding acids by treatment with sodium nitrite and sulphuric acid.

In the case of ethyldecyldodecylacetic acid a separation from admixed decyldodecylacetic acid could be effected by partial hydrolysis of the ester, the trisubstituted ester remaining practically unchanged after boiling for 5 hours with excess of 25% alcoholic potassium hydroxide, whereas the disubstituted ester was all hydrolysed under these conditions.

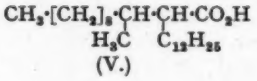
The m. p.'s given below are those which were found immediately after the preparations, because in several cases the m. p. rose on keeping. The phenomenon may be due to polymorphism but suggests imperfect orientation of the molecule in the newly formed crystals and a slow process of better marshalling of the long chains in the solid state.

| | | M.p. | M.p. of amide. |
|---|---|---|---|
| Methyldecyldodecylacetic acid | $C_{25}H_{50}O_2$ ..... | 41° | 42° |
| Ethyldecyldodecylacetic acid | $C_{26}H_{52}O_2$ ..... | 27—28 | Liquid |
| Methylheptyltetradecylacetic acid | $C_{24}H_{48}O_2$ ..... | 44 | 30—31 |
| Methyldiheptylacetic acid | $C_{17}H_{34}O_2$ ..... | Liquid | Liquid |
| Phthioic acid | $C_{26}H_{52}O_2$ ..... | 20—21 | 45 |

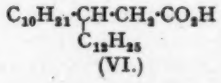
No close relation of the synthetic acids with phthioic acid can be deduced from these figures. Methyldecyldodecylacetic acid forms an amide with m. p. similar to that of phthioic amide but has a much higher melting point than phthioic acid. Ethyldecyldodecylacetic acid forms a liquid amide and differs from phthioic acid in the fact that its ester is difficult to hydrolyse.

A characteristic property of phthioic acid according to Stenhagen and Ställberg (*loc. cit.*) is that it forms unimolecular layers collapsing on compression at an area of about 38 A.$^2$. Film measurements with the above synthetic acids showed, however, that their monolayers cannot be compressed below about 65 A.$^2$ without collapse, and in this respect behave in nearly the same way as the disubstituted acetic acids. The same result was obtained with monolayer films of *methyl*-n-*nonyl*-n-*dodecylcarbinol* (prepared from methyl nonyl ketone and dodecylmagnesium bromide). These and other film measurements will be described in detail in a later communication. Phthioic acid is optically active, and this fact introduces some dubiety into the comparisons. Unfortunately we have been unable to resolve methyldecyldodecylacetic acid and the study of the film properties of an optically active member of this series is still desirable.

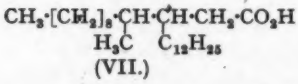
Branched-chain acids of the disubstituted-acetic acid and of the di- and tri-substituted-propionic acid types have also been synthesised in order to examine their properties in films.



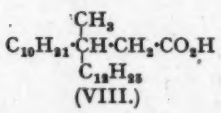
(V.)



(VI.)



(VII.)



(VIII.)

3-*Methyl*-2-n-*dodecyl-lauric acid* (V) was obtained by alkylation of ethyl malonate, *sec.*-undecyl bromide and *n*-dodecyl bromide being used.

β-n-*Decyl*-β-n-*dodecylpropionic acid* (VI) was obtained from decyldodecylacetic acid by the homologation reaction of Arndt and Eistert (*Ber.*, 1935, **68**, 200; 1936, **69**, 1074). 4-*Methyl*-3-n-*dodecyltridecoic acid* (VII) and β-*methyl*-β-n-*decyl*-β-n-*dodecylpropionic acid* (VIII) were prepared in the same way from 3-methyl-2-dodecyl-lauric acid (V) and methyldecyldodecylacetic acid (I). Monolayer films of these acids had collapse areas similar to those of the trisubstituted acetic acids.

The failure to obtain, with any of the above acids, surface areas similar to those occupied by films of phthioic acid suggested the desirability of investigating branched-chain acids with a long-chain substituent further removed from the carboxyl group. It was thought possible that an acid of the type $CHR_1R_2{\cdot}[CH_2]_x{\cdot}CO_2H$ might form monolayer films compressible to a smaller area.

Taking into consideration the *X*-ray results of Stenhagen, which indicated a chain-length of about 15 carbon atoms for phthioic acid, and also the relatively high molecular rotation of phthioic acid, suggesting, as pointed out by Spielman and Anderson (*loc. cit.*), an asymmetric carbon atom near the carboxyl group, the

preparation of 2-*methyl*-5-n-*decylpentadecoic acid* was undertaken. It was obtained by the following sequence of reactions:

$$(C_{10}H_{21})_2CO \xrightarrow{\text{ethyl bromoacetate, Zn}} (C_{10}H_{21})_2C(OH)\cdot CH_2\cdot CO_2Et \xrightarrow{SOCl_2,\ \text{pyridine}} (C_{10}H_{21})_2C{:}CH\cdot CO_2Et \xrightarrow{H_2,Ni} (C_{10}H_{21})_2CH\cdot CH_2\cdot CO_2Et \xrightarrow{Na,BuOH} (C_{10}H_{21})_2CH\cdot CH_2\cdot CH_2\cdot OH \xrightarrow[P]{\text{iodine}} (C_{10}H_{21})_2CH\cdot CH_2\cdot CH_2I \xrightarrow{\text{ethyl sodiomalonate}}$$

$$(C_{10}H_{21})_2CH\cdot CH_2\cdot CH_2\cdot CH(CO_2Et)_2 \xrightarrow{NaOEt,MeI} (C_{10}H_{21})_2CH\cdot CH_2\cdot CH_2\cdot CMe(CO_2Et)_2 \xrightarrow{\text{hydrolysis, decarboxylation}}$$

$$(C_{10}H_{21})_2CH\cdot CH_2\cdot CH_2\cdot CHMe\cdot CO_2H \text{ (IX.)}$$

Monolayer films of 2-methyl-5-decylpentadecoic acid (IX) showed similar properties to those of the acids previously described; they could not be compressed without collapse below an area of about 64 A.$^2$.

Our conclusions may be summarised by the statement that monolayer films of branched-chain acids containing two long chains cannot be compressed below an area of about 60 A.$^2$ no matter where the second chain may be in relation to the carboxyl group, and whether they contain a quaternary carbon atom or not. This difference from the behaviour of films of phthioic acid as reported by Stenhagen and Ställberg (*loc. cit.*) seems to rule out the possibility that the phthioic acid molecule has an overall length corresponding to a 15 carbon atom chain, the remaining carbon atoms being mainly arranged in a second long chain.

The alternative view that phthioic acid is a long-chain acid containing several short branches (methyl groups), as originally suggested by Spielman and Anderson, is not easily reconciled with the results obtained by Stenhagen and Ställberg by *X*-ray examination of barium phthioate. These authors also point out that 3 : 7 : 11 : 15-tetramethylhexadecoic acid (phytanic acid) forms films behaving differently from those of phthioic acid.

From a recent communication of Stenhagen and Ställberg (*J. Biol. Chem.*, 1943, **148**, 685) it appears, however, that in the case of branched-chain acids the long crystal spacings, as determined by *X*-rays, are considerably shorter than in the case of the normal acids, the values found being 40·5, 51·0, and 56·0 A. for the 2-methyl-substituted $C_{21}$-, $C_{25}$-, and $C_{27}$-acids respectively, and 45·7 A. for the 10-methyl-substituted $C_{24}$-acid, compared with values of 56·3, 66·0, and 70·8 A. for the normal $C_{20}$-, $C_{24}$-, and $C_{26}$-acids. These authors point out that the long chains in these branched-chain acids are tilted, thus differing from normal-chain acids, which crystallise with vertical chains. It is, therefore, doubtful whether the long spacings of 35 A. found by the same authors for phthioic acid do necessarily require an assignment of a chain length of about 15 carbon atoms.

The film properties of $C_{26}$-acids with several short branches ($CH_3$) are unknown, no such acid having yet been synthesised. They might be quite different from those of lower homologues, such as phytanic acid, which, as mentioned above, forms films differing from those of phthioic acid.

No definite conclusions are possible until such $C_{26}$-acids with a number of short branches have been examined and work with this object in view will be undertaken when opportunity offers.

According to Wagner-Jauregg (*loc. cit.*), tuberculostearic acid, with two methyl groups, gives 1·4CMe in the Kuhn–Roth estimation and phthioic acid gives 2·4CMe. Hence we may surmise that phthioic acid contains at least three methyl groups and certainly not more than four. Analogy suggests a dimethyl-*n*-tetracosoic acid with one methyl group in the same position relative to carboxyl as in tuberculostearic acid.

## Experimental.

*Methyl*-n-*decyl*-n-*dodecylacetic Acid* (I).—Ethyl *n*-decylmalonate, b. p. 144—146°/0·15 mm., was obtained in 85% yield from ethyl malonate (144 g.), *n*-decyl bromide (62 g.), sodium (11 g.), a little sodium iodide, and alcohol (120 c.c.) by refluxing the mixture for 7 hours. It was converted into ethyl *n*-decyl-*n*-dodecylmalonate, b. p. 214—216°/0·25 mm., in 70% yield by refluxing its sodio-compound with *n*-dodecyl bromide (59·5 g.), a little sodium iodide, and alcohol (70 c.c.) for 12 hours; the recovered ethyl *n*-decylmalonate and *n*-dodecyl bromide, worked up in the same way, gave a further 10 g. of the ester (total yield, 80%). On hydrolysis with excess of 25% alcoholic potassium hydroxide and subsequent acidification *n*-decyl-*n*-dodecylmalonic acid was obtained in almost quantitative yield. This was partly decarboxylated by heating for 10 minutes at 100° under diminished pressure and then for 10 minutes at 100—105°/<1 mm. *n*-Decyl-*n*-dodecylacetic acid distilled, b. p. 224—226°/0·1 mm., as a colourless oil which quickly crystallised; m. p. 44—45° (Found: C, 78·8; H, 13·2. Calc. for $C_{24}H_{48}O_2$: C, 78·3; H, 13·0%). After crystallisation from acetone or acetic acid it had m. p. 47° (Stenhagen, *Trans. Faraday Soc.*, 1940, **36**, 597, gives the same m. p.). Its amide had m. p. 112·5°. This acid was converted into its methyl ester, b. p. 198—200°/0·25 mm., by refluxing for 5 hours with 10% methanolic sulphuric acid.

Methyl decyldodecylacetate (21 g., 0·055 mol.) was added to a freshly prepared solution of sodium triphenylmethyl (from 21 g., 0·075 mol., of triphenylchloromethane and 500 g. of 1% sodium amalgam) in dry ether (450 c.c.), the whole operation being conducted under pure nitrogen. The mixture was shaken and kept for 4 hours. Methyl iodide (30 g.) was then added and after 20 hours water was added, and the product isolated by means of ether and obtained as a pale yellow oil (16 g.), b. p. 196—200°/0·2 mm. It was refluxed for 5 hours with an excess of 25% alcoholic potassium hydroxide, the acid liberated and converted into its lead salt by solution in alcohol, neutralisation with alcoholic potassium hydroxide and precipitation with lead acetate. The lead salt was extracted with alcohol; it yielded on treatment with dilute nitric acid an acidic product, m. p. 34—35°, from acetone. This was converted into its amide by treatment with an excess of thionyl chloride and addition of the resulting acid chloride to concentrated aqueous ammonia. On fractional crystallisation from methanol or acetone two products were separated, namely, decyldodecylacetamide, m. p. 112·5°, and the more soluble *methyldecyldodecylacetamide* (about 8 g.), which after repeated crystallisations from acetone and finally from methanol had m. p. 42° (Found: C, 79·0; H, 13·4; N, 3·7. $C_{25}H_{51}ON$ requires C, 78·7; H, 13·4; N, 3·7%). This amide was dissolved in 10 times its weight of concentrated sulphuric acid; an excess of 10% aqueous sodium nitrite was gradually added with cooling in ice. The mixture was kept overnight and diluted with water, and the resulting *methyldecyldodecylacetic acid* isolated by means of ether. After crystallisation from acetone it

had m. p. 41°. After 8 months the m. p. rose to 44·5° (Found : C, 78·4, 78·3; H, 12·9, 13·1; no N. $C_{25}H_{50}O_2$ requires C, 78·5; H, 13·1%).

A number of unsuccessful attempts were made to resolve this acid in order to investigate the film properties of the optically active trialkylacetic acid, which might perhaps differ from those of the *dl*-acid. No crystalline salts could be obtained with quinine, cinchonine, strychnine or brucine, and the acids from the oily products which separated showed no optical activity. In the case of *tert.*-alcohols containing the hydroxyl group attached to the asymmetric carbon atom, Kenyon and Priston (J., 1925, **127**, 1476) failed to effect any resolution.

*Ethyl*-n-*decyl*-n-*dodecylacetic Acid* (II).—Methyl *n*-decyl-*n*-dodecylacetate (7 g., 0·018 mol.) was treated with an ethereal solution of sodium triphenylmethyl (from 7 g., 0·025 mol., of triphenylchloromethane and 170 g. of 1% sodium amalgam in 150 c.c. of dry ether). Ethyl iodide (10 g.) was added after 3½ hours, and the mixture worked up as already described for the lower homologue. The product (3·7 g.), b. p. 200—202°/0·2 mm., was refluxed for 5 hours with an excess of 25% alcoholic potassium hydroxide. Treatment of the free acid with lead acetate yielded only a small quantity (1 g.) of crude *n*-decyl-*n*-dodecylacetic acid giving an amide of m. p. 112·5°. The unhydrolysed ester (2·5 g.), which was recovered from the alcoholic filtrate from the lead salt, furnished, on refluxing for 7 hours with *n*-propyl-alcoholic potassium hydroxide, an oily acidic product. This was purified through its lead salt (1·9 g.) and converted into the amide by the usual method. Repeated crystallisation from acetone and methanol afforded a small quantity of *n*-decyl-*n*-dodecylacetamide, m. p. 112·5°. When the mother liquors were concentrated and cooled, a low-melting product crystallised, which liquefied at once on removal from the refrigerator. After repeated extractions with small quantities of chilled acetone, it was converted into the *acid* by treatment with sodium nitrite and sulphuric acid. On distillation under high vacuum, a viscous oil (0·8 g.) was obtained which slowly crystallised, m. p. 27—28°, from acetone. After some weeks it melted at 31° (Found : C, 78·5; H, 13·0. $C_{26}H_{52}O_2$ requires C, 78·8; H, 13·1%). The *amide* obtained from this specimen was a viscous oil (Found : C, 78·9; H, 13·2; N, 3·5. $C_{26}H_{53}ON$ requires C, 79·0; H, 13·4; N, 3·5%).

*Methyl*-n-*heptyl*-n-*tetradecylacetic Acid* (III).—The preparation of this acid was carried out like that of methyl-*n*-decyl-*n*-dodecylacetic acid. n-*Heptyl*-n-*tetradecylacetic acid*, which was obtained by the malonic ester method using *n*-heptyl bromide and *n*-tetradecyl bromide, had m. p. 42° (Found : C, 77·8; H, 12·9. $C_{23}H_{46}O_2$ requires C, 78·0; H, 13·0). The methyl ester of this acid gave, by interaction with sodium triphenylmethyl and methyl iodide and hydrolysis of the resulting ester, the crude trisubstituted acid (m. p. 39·5°), which was converted into the amide in order to separate it from some unchanged disubstituted acid. The amide, m. p. 30—31°, after repeated crystallisations from acetone and methanol, yielded by treatment with sodium nitrite and sulphuric acid *methyl*-n-*heptyl*-n-*tetradecylacetic acid*, m. p. 44° after recrystallisation from acetone (Found : C, 78·0; H, 13·2. $C_{24}H_{48}O_2$ requires C, 78·3; H, 13·0%).

*Methyldi*-n-*heptylacetic Acid* (IV).—Di-*n*-heptylacetic acid, m. p. 26—27°, was prepared from *n*-heptyl bromide and malonic ester (Found : C, 74·9; H, 12·2. Calc. for $C_{16}H_{32}O_2$ : C, 75·0; H, 12·5%). Its methyl ester (33 g.) furnished, by interaction with excess of sodium triphenylmethyl and methyl iodide, a colourless oil (27 g.), b. p. 132—136°/0·15 mm., which was hydrolysed with alcoholic potassium hydroxide. The product (22 g.) obtained on acidification, b. p. 162—168°/0·1 mm., was converted into the amide by means of thionyl chloride and ammonia. Repeated treatment with acetone separated a crystalline product, m. p. 107—108° (amide of unchanged disubstituted acid). The product remaining in solution furnished after repeated distillations *methyldi*-n-*heptylacetamide* as a colourless, very viscous oil (9·8 g.), b. p. 181—182°/0·2 mm. (Found : C, 75·5; H, 12·9; N, 5·2. $C_{17}H_{35}ON$ requires C, 75·8; H, 13·0; N, 5·2%). It was converted into the acid by treatment with sodium nitrite and sulphuric acid. This was separated from some unchanged amide by converting it into its methyl ester, b. p. 172—173°/*ca.* 12 mm., and furnished on hydrolysis *methyldi*-n-*heptylacetic acid* (5·4 g.), b. p. 171—171·5°/0·2 mm., as a viscous oil (Found : C, 76·1; H, 12·7. $C_{17}H_{34}O_2$ requires C, 75·5; H, 12·6%).

*Methyl*-n-*nonyl*-n-*dodecylcarbinol*.—Methyl nonyl ketone (25 g.) was gradually added to a Grignard solution, prepared from *n*-dodecyl bromide (37 g.) and magnesium (3·5 g.) in ether (40 c.c.), with stirring below 10°. The chief product was a colourless oil (21 g.), b. p. 200—204°/*ca.* 0·2 mm. (Found : C, 81·0; H, 14·0. $C_{32}H_{66}O$ requires C, 81·2; H, 14·1%).

3-*Methyl*-2-n-*dodecyl*-*lauric Acid* (V).—Ethyl *sec.*-undecylmalonate, b. p. 180—182°/18 mm., was obtained in 70% yield from ethyl malonate (64 g.), *sec.*-undecyl bromide (35 g.), sodium (5 g.), some sodium iodide, and alcohol (75 c.c.) by refluxing the mixture for 7 hours. This was converted into *ethyl* sec.-*undecyl*-n-*dodecylmalonate*, b. p. 210—212°/0·16 mm., in 50% yield by refluxing its sodio-derivative with *n*-dodecyl bromide (17·5 g.) and some sodium iodide in xylene (30 c.c.) for 24 hours (Found : C, 74·6; H, 12·0. $C_{39}H_{74}O_4$ requires C, 74·7; H, 12·0%). It was hydrolysed by refluxing it repeatedly with *n*-propyl-alcoholic potassium hydroxide. The product obtained on acidification was decarboxylated under reduced pressure. On distillation, a colourless oil (9 g.), b. p. 228—230°/0·3 mm., was obtained, which crystallised on keeping (Found : C, 78·9; H, 13·1. $C_{25}H_{50}O_2$ requires C, 78·5; H, 13·1%). It melted at 67° after recrystallisation from acetone and furnished an amide, m. p. 102—103°.

*β*-n-*Decyl*-*β*-n-*dodecylpropionic Acid* (VI).—*n*-Decyl-*n*-dodecylacetic acid (6 g.) was converted by means of thionyl chloride into its chloride, and this treated with ethereal diazomethane. The diazo-ketone was obtained in yellow crystals after removal of the ether and excess of diazomethane under reduced pressure at room temperature. It was dissolved in warm methanol (50 c.c.), and the solution heated on a steam-bath while a methanolic suspension of silver oxide (from 2 g. of silver nitrate) was gradually added during about 1 hour; the mixture was then refluxed for 1 hour. The resulting methyl ester, b. p. 212—214°/0·25 mm., furnished by hydrolysis with alcoholic potassium hydroxide and subsequent acidification the required *acid* as a viscous oil (Found : C, 78·7; H, 13·1. $C_{38}H_{50}O_2$ requires C, 78·5; H, 13·1%). It solidified at 0°, but melted at room temperature. After several weeks it melted at 26·5°; amide, m. p. 55°.

4-*Methyl*-3-n-*dodecyltridecoic Acid* (VII).—3-Methyl-2-*n*-dodecyl-lauric acid (5 g.) was converted into its chloride, which was added to an ethereal solution of diazomethane. The resulting diazo-ketone yielded by treatment with silver oxide and ethyl alcohol the homologous ethyl ester. This was hydrolysed with alcoholic potassium hydroxide; the *product* obtained on acidification distilled as a colourless oil (3 g.), b. p. 209—210°/0·1 mm. (Found : C, 78·8; H, 13·1. $C_{26}H_{52}O_2$ requires C, 78·8; H, 13·2%). It deposited on standing traces of a crystalline material which seemed to be unchanged 3-methyl-2-dodecyl-lauric acid; its amide was a liquid.

*β-Methyl*-*β*-n-*decyl*-*β*-n-*dodecylpropionic Acid* (VIII).—Methyl-*n*-decyl-*n*-dodecylacetic acid was converted into its chloride, then into a diazoketone in the same way as described in the previous cases. The resulting diazo-ketone, m. p. 36° from methanol, yielded by, treatment with methanol and silver oxide, *methyl β-methyl-β-decyl-β-dodecylpropionate*, b. p. 196—197°/0·2 mm. (Found : C, 79·6; H, 12·9. $C_{27}H_{54}O_2$ requires C, 79·0; H, 13·2%). On hydrolysis with alcoholic potassium hydroxide and subsequent acidification *β-methyl*-*β*-n-*decyl*-*β*-n-*dodecylpropionic acid* was obtained as a colourless viscous oil (Found : C, 78·9; H, 13·1. $C_{26}H_{52}O_2$ requires C, 78·8; H, 13·1%). It furnished a liquid *amide* (Found : C, 79·4; H, 12·9; N, 3·4. $C_{26}H_{53}ON$ requires C, 79·0; H, 13·4; N, 3·5%).

2-*Methyl*-5-n-*decylpentadecoic Acid* (IX).—A mixture of di-*n*-decyl ketone (40 g., prepared by pyrogenic decomposition of lead undecoate), zinc filings (8 g.), ethyl bromoacetate (22·5 g.), dry ether (75 c.c.), and benzene (75 c.c.) was heated on a steam-bath with stirring. After about 3 hours further quantities of zinc (6 g.) and ethyl bromoacetate (12 g.) were introduced, and the heating continued for a further 3 hours. The solution was then decanted from unreacted zinc into a mixture of ice and water containing a small quantity of acetic acid. The benzene–ether layer was repeatedly

washed with 10% aqueous acetic acid, some dilute aqueous ammonia, and water, and dried with sodium sulphate. Since in a preliminary experiment the product was found to decompose on distillation with formation of didecyl ketone, it was not isolated. The above benzene–ether solution was concentrated under reduced pressure, pyridine (32 g.) added, and thionyl chloride (34 g.) gradually introduced while the ice-cold mixture was stirred. It was kept overnight, then poured slowly into ice-water, and the product washed with dilute hydrochloric acid, dried, and distilled. *Ethyl* 3-*decyl*-$\Delta^3$-*tridecenoate* (36 g.) was obtained as a slightly coloured oil, b. p. 192—196°/0·4 mm., $n_D^{19°}$ 1·4600 (Found: C, 78·6; H, 12·0. $C_{25}H_{48}O_2$ requires C, 78·9; H, 12·6%).

Before hydrogenation, the above ester, dissolved in light petroleum (120 c.c., b. p. 60—80°), was filtered through a column of charcoal and, after removal of the solvent, refluxed in alcoholic solution with Raney nickel in order to remove any catalyst poisons. It was hydrogenated in alcoholic solution with Raney nickel at 40—60°/60 atm. *Ethyl* 3-*decyltridecoate* (29·5 g.) was obtained as a colourless oil, b. p. 179—181°/0·2 mm., $n_D^{19°}$ 1·4539 (Found: C, 78·6; H, 12·8. $C_{25}H_{50}O_2$ requires C, 78·5; H, 13·1 g.).

The reduction of this ester to the corresponding alcohol was effected by the method of Bleyberg and Ulrich (*Ber.*, 1931, **64**, 2504), light petroleum (260 c.c., b. p. 60—80°), sodium (35 g.), and butyl alcohol (160 c.c.) being used. A considerable quantity of high-boiling product was formed, presumably owing to self-condensation of the ester. 3-*Decyltridecanol* (8 g.) was obtained as a viscous oil, b. p. 163—165°/0·15 mm., $n_D^{21°}$ 1·4608 (Found: C, 81·3; H, 13·7. $C_{23}H_{48}O$ requires C, 81·2; H, 14·1%). 7 G. of 3-decyltridecoic acid were recovered.

The above alcohol (8 g.) was converted into its iodide by heating with red phosphorus (0·26 g.) and iodine (3 g.) at 180° for 1½ hours. This was kept overnight with a solution of ethyl sodiomalonate (from 12 g. of malonic ester and 0·81 g. of sodium) in alcohol (10 c.c.); the mixture was then refluxed with stirring for 4 hours. *Ethyl* (3-*decyltridecyl*)-*malonate* (6 g.), b. p. 221—224°/0·45 mm., $n_D^{22°}$ 1·4540, was obtained as a colourless oil (Found: C, 74·7; H, 12·0. $C_{30}H_{58}O_4$ requires C, 74·7; H, 12·0%).

The above alkylated malonic ester was converted into its sodio-derivative by means of sodium (0·28 g.) in alcohol (15 c.c.); excess of methyl iodide was then added, and the mixture refluxed for 3 hours with stirring while further small quantities of methyl iodide were introduced at intervals. The product was hydrolysed with alcoholic potassium hydroxide. On acidification, followed by decarboxylation, 2-*methyl*-5-*decylpentadecoic acid* (2·4 g.) was obtained as a viscous oil, $n_D^{23°}$ 1·4579, becoming turbid on cooling with ice (Found: C, 78·3; H, 13·1. $C_{26}H_{52}O_2$ requires C, 78·8; H, 13·1%).

The authors thank the Therapeutic Research Corporation of Great Britain for financial assistance.

DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, September 6th*, 1943.]

---

## 166. *The Amylolytic Degradation of Starch.*

By W. N. HAWORTH, H. KITCHEN, and S. PEAT.

It is shown that β-amylase hydrolyses the amylopectin component of starch with the formation of maltose and a limit dextrin: dextrin-A or α-amylodextrin. Dextrin-A is not susceptible of further attack by β-amylase until it has been "sensitised" by contact with salivary amylase. Thereafter the action of β-amylase continues until a second resting stage—dextrin-B—is reached. Dextrin-B is not further hydrolysed by β-amylase and is not sensitised by saliva. It is, however, hydrolysed by salivary amylase with the production of maltose and dextrin-C. This dextrin is slowly hydrolysed by pancreatic amylase with the formation of dextrin-D. End-group assay on the methylated dextrins indicates that the unit chain-lengths are 7—8 (dextrin-B), 5—6 (dextrin-C), and 4—5 (dextrin-D).

The mechanism of amylolysis is explicable on the basis of the simple laminated formulation of the structure of starch propounded by Haworth and Hirst, if it be assumed (i) that the impediment to β-amylase action is represented by the polymeric links which unite the unit chains; (ii) that the polymeric links are ruptured by an enzymic constituent of saliva and of malt α-amylase; and (iii) that the unit chains so liberated immediately recombine with the formation of new polymeric (*i.e.*, 1 : 6-α-glucosidic) links with a different orientation of position on the respective chains.

It is not necessary to postulate a complex, highly ramified structure for amylopectin, such as that proposed by K. H. Meyer, to explain the facts of amylolysis.

THE various dextrins produced by the amylolysis of starch have been named on no logical basis but rather according to the predilections of individual investigators. Thus the residual dextrin obtained by the action of β-amylase on starch has been named α-amylodextrin by Baker and erythrogranulose by Wijsman. In this paper are described a series of limit dextrins which are closely interrelated in that they are produced by the systematic and progressive enzyme degradation of starch. We propose, therefore, to name these dextrin-A, dextrin-B, dextrin-C, etc. Dextrin-A is identical with α-amylodextrin and was in fact so named by us in an earlier paper (Haworth, Hirst, Kitchen, and Peat, J., 1937, 791).

In the earlier paper the limit dextrin which resulted from the completed action of β-amylase on potato starch was described. This limit dextrin (α-amylodextrin, erythrogranulose, dextrin-A) represents 40% by weight of the original starch, the remaining 60% of which appears as maltose. Dextrin-A was shown to have an apparent unit chain length (determined by end-group assay) of 11—12 glucose members and to be resistant to further attack by β-amylase.

It is known that the obstruction to the action of β-amylase shown by dextrin-A may be simply removed by submitting the dextrin to treatment with water in an autoclave at 120°, or to the action of malt α-amylase (cf. Hanes, *Canadian J. Res.*, 1935, **13**, *B*, 185). In the further degradation of dextrin-A, we have adopted the second method and have used saliva as the enzyme source.

Preliminary experiments demonstrated that the susceptibility of dextrin-A to hydrolytic attack by β-amylase was restored when salivary amylase was allowed to act upon the dextrin for even a few seconds.

Dextrin-A, "sensitised" by contact with salivary amylase, was now submitted to the action of β-amylase at 38° for a prolonged period. A second limit dextrin, dextrin-B, was thus produced and this represented

58% by weight of dextrin-A. The only other product of hydrolysis was maltose, which was isolated as crystalline maltose hydrate, the weight of which represented 38% of dextrin-A.

Dextrin-B was easily methylated with methyl sulphate and sodium hydroxide and end-group assay on the methylated derivative indicated for the dextrin a unit chain-length of 7—8 glucose members.

Dextrin-B was not further hydrolysed by β-amylase. Moreover, it was not " sensitised " by the momentary action of salivary amylase, in the sense that the latter enzyme did not remove the impediment to the further action of β-amylase. Nevertheless, the salivary amylase itself effected further hydrolysis of dextrin-B whereby crystalline maltose (27%) and limit dextrin-C (67%) were produced. End-group assay of the methylated dextrin-C showed its unit chain to consist of 5—6 glucose members. Dextrin-C was not further hydrolysed by β-amylase, salivary amylase, malt amylase (α and β) or taka-diastase. It was, however, slowly attacked in the presence of a purified commercial pancreatic amylase. Dextrin-D (80% of dextrin-C) was thus obtained, together with a sugar which, by analytical procedure only, appeared to be maltose.* The chain-length of this dextrin, as determined by assay of the methylated derivative, was 4—5 glucose units.

The properties of the dextrins formed by the amylolytic breakdown of starch are given in Tables I and II, together with those of potato starch and a commercial acid-solubilised starch.

TABLE I.

*Degradation Products of Potato Starch.*

| | Potato starch.[1] | Soluble starch.[1] | Dextrin-A (α-amylo-dextrin).[2] | Dextrin-B. | Dextrin-C. | Dextrin-D. |
|---|---|---|---|---|---|---|
| Solubility | Boiling $H_2O$ | Hot $H_2O$ | Hot $H_2O$ | Cold $H_2O$ | Cold $H_2O$ | Cold $H_2O$ |
| Retrogrades? | Yes | Yes | Yes | No | No | No |
| Reducing? (Cu number) | Slightly (0·04) | Slightly (0·2) | Slightly | Slightly | Yes | Yes |
| Iodine value | 1·1 | 1·3 | 2·7 | 8 | 13 | 14·2 |
| Iodine colour | Blue | Blue | Purple | Red | Nil | Nil |
| $[\alpha]_D$ in $H_2O$ | +187° | — | +167° | +156° | +148° | +116° |
| $[\alpha]_D$ in 5% NaOH | +150° | +148° | +133° | +127° | +116° | {+111° →+ 95° |
| P content % (as $P_2O_5$) | 0·14 | 0·22 | 0·40 | 0·59 | 1·0 | 1·25 |

TABLE II.

*Methylated Products.*

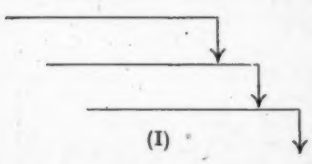
| | Potato starch.[1] | Soluble starch.[1] | Dextrin-A.[2] | Dextrin-B. | Dextrin-C. | Dextrin-D. |
|---|---|---|---|---|---|---|
| OMe % | 44·5 | 44·0 | 44·0 | 43·1 | 44·5 | 46·0 |
| $[\alpha]_D$ in $CHCl_3$ | +205° | +204° | +194° | +185° | +182° | +176° |
| $\eta_{sp./c}$ in *m*-cresol | 0·9 | 0·5 | 0·43 | 0·075 | 0·09 | 0·10 |
| Mol. wt. (osmotic pressure) | — | 28,000[3] | 79,000[4] | 16,000[4] | — | — |
| Chain-length by end group assay (glucose units) | 24—26 | 27—28 | 11—12 | 7—8 | 5—6 | 4—5 |

[1] H. Kitchen, Ph.D. Thesis, Birmingham, 1937. [2] Haworth, Hirst, Kitchen, and Peat, *loc. cit.* [3] Carter and Record, *Chem. and Ind.*, 1936, 218. [4] W. T. Chambers, Ph.D. Thesis, Birmingham, 1939.

## DISCUSSION.

The immediate problem is to reconcile the facts of amylolysis with the structure which has been assigned to starch on chemical grounds.

The laminated formulation (I) was proposed for starch in 1937 (Haworth, Hirst, and Isherwood, J., 1937, 577), based on the model we had already suggested as best representing the constitution of xylan (Haworth, Hirst, and Oliver, J., 1934, 1917).



(I)

The observations now recorded were published in thesis form in 1937 (H. Kitchen, Ph.D. Thesis, University of Birmingham) and we have long had in mind the possibility that the impediment to β-amylase action is presented by the linkages [represented by the arrow heads in (I)] which unite the basal chains. No novelty is claimed for this view of the nature of the obstruction to the action of β-amylase, and it has, of course, occurred to others (cf. Hanes, *New Phytol.*, 1937, **36**, 229).

Wider publication of our results is necessitated by the appearance of a series of papers by K. H. Meyer and his associates describing investigations which follow substantially the same lines as our own (see *Helv. Chim. Acta*, 1940, **23**, 875). Dextrin-A (called dextrin-I by Meyer) was treated for an arbitrary period (14 hours) with yeast maltase, whereby glucose (17%) was liberated and dextrin-II (75%) formed. Dextrin-II was now susceptible to the action of β-amylase, which effected further hydrolysis to dextrin-III (64% of dextrin-I). It appears likely that Meyer's dextrin-III and our dextrin-B are identical in that both represent approximately the same fraction by weight of dextrin-A and both give a red colour with iodine. No end-group assay of dextrin-III is reported, so a comparison in this respect is not possible.

* In all other cases the weight of isolated crystalline maltose is quoted. We do not favour the facile dependence on titration methods for the estimation of maltose in solution, since the result may be due to more than one reducing sugar.

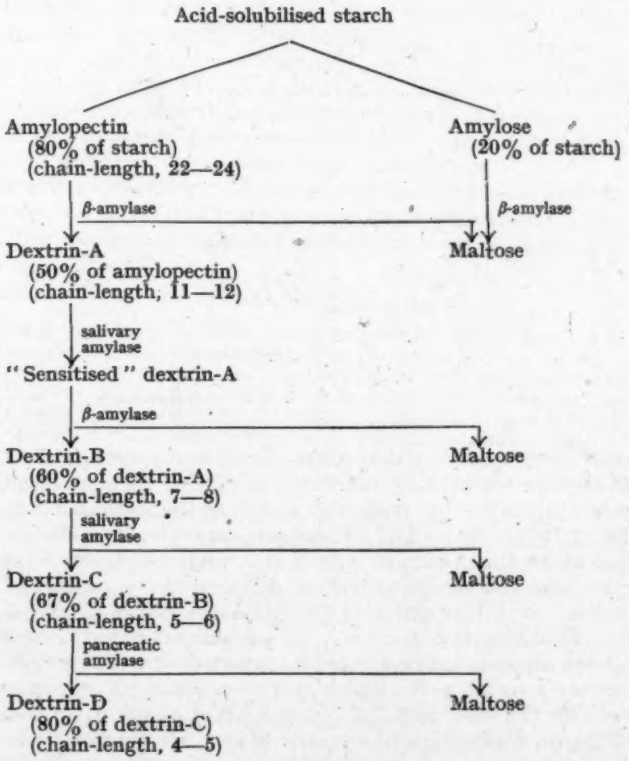
Natural starch is now considered to be a mixture of two components which are different in respect of the length of their unit chains (K. H. Meyer *et al.*, *loc. cit.*; Hassid and McCready, *J. Amer. Chem. Soc.*, **1943**, **65**, 1157) and of the degree of aggregation of these chains. The short-chain, highly aggregated component is described as " amylopectin "; the long-chain component as " amylose."

In the experiments described above, Meyer used amylopectin as substrate for the amylases, whereas we used an acid-solubilised whole starch. Inasmuch as amylose is completely hydrolysed to maltose by β-amylase, it is clear that our dextrin-A is derived, like Meyer's dextrin-I, entirely from the amylopectin component, which constitutes, according to the most recent evidence, 80% of the whole. With the readjustment of the weight yield of dextrin-A in accordance with this development, our observations may be summarised as in Table III.

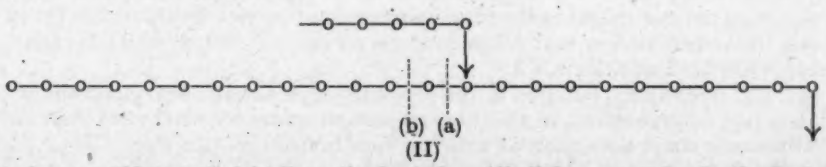
If it be accepted that the impediment to β-amylase action on amylopectin lies in the polymeric linkages between unit chains, it is necessary to assume that such linkages unite the reducing end-group of one chain with, as an average, the middle glucose member of the second chain, for otherwise it is not possible to account for the formation in 50% weight yield of a dextrin with a unit chain of half the length. It must be clearly understood that we are necessarily speaking in terms of averages only. The figures quoted for unit chain-lengths are statistical averages and the actual length of any one unit chain may be widely different from the mean—how widely we have no way of judging at present. A similar reservation attaches to the statement concerning the position of the polymeric bonds in amylopectin.

β-Amylase effects the progressive removal of maltose residues from the non-reducing ends of the unit chains and it is to be expected that this activity will continue so long as there remain two glucose units mutually combined in the configuration of maltose and united by a 1 : 4-α-glucosidic link (at which the actual fission will take place) to the remainder of the chain. The glucose unit involved in the polymeric link clearly cannot

TABLE III.




form part of a free maltose configuration, because it is substituted at $C_6$ and therefore β-amylase hydrolysis will not pass along the chain beyond the polymeric link. This is illustrated in (II), which shows, diagrammatically, an intermediate chain-unit in amylopectin.

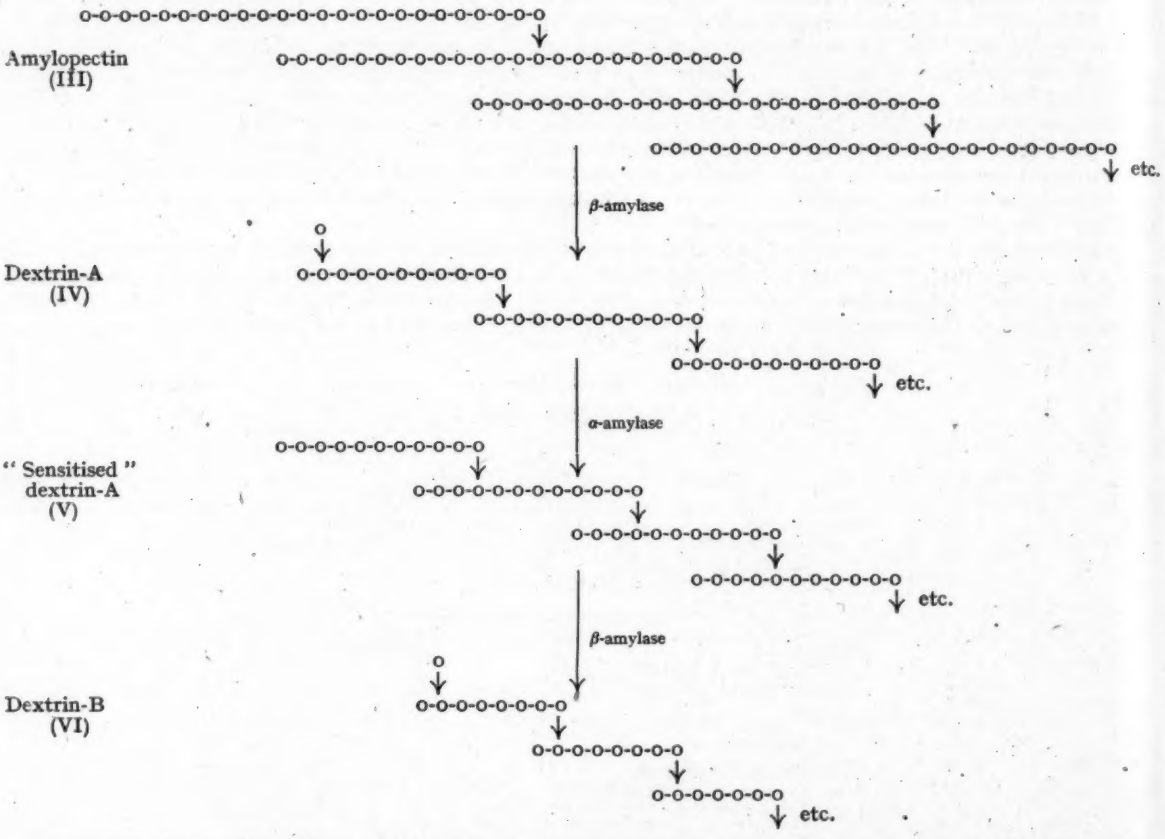



(II)

(Circles represent glucose residues; straight lines, the 1 : 4-glucosidic links; arrow heads, the 1 : 6-polymeric bonds.)

It is furthermore apparent that the final scission must take place at (*b*) and not at (*a*), for otherwise there would be no tetrahydroxy terminal group left in the chain, which is now a chain-unit of dextrin-A, and end-group assay would indicate only one end-group in the whole molecule of the dextrin. As one glucose residue in every 12 is an end-group, the dextrin must, like starch, be constituted of unit chains aggregated by polymeric bonds. This could not be the case if β-amylase carried hydrolysis to the point (*a*).

On this view, the degradation of amylopectin to dextrin-A is shown diagrammatically by the change (III) ⟶ (IV).




This view implies that the polymeric linkages are not disturbed and it is to be expected that dextrin-A will possess a degree of aggregation of the same order as that of the amylopectin from which it is derived. Dextrin-A is in fact highly aggregated, the molecular weight of the methylated dextrin determined by osmotic pressure measurement being 79,000 (Table II). This figure corresponds to 400 glucose residues.

It is in the conversion of dextrin-A into dextrin-B that real difficulties of interpretation arise. It would seem that salivary amylase (and also the α-glucosidase of Meyer, *loc. cit.*) attacks the 1 : 6-α-glucosidic linkages which constitute the " block " to further action of β-amylase on dextrin-A. Whereas α-glucosidase in bringing about the same result is allowed to act on dextrin-A for a prolonged period and causes the liberation of glucose at the same time, the salivary amylase appears to act instantaneously. In fact, its action on dextrin-A forcibly recalls its action in liquefying a starch paste, which also takes place almost instantaneously.

There is some evidence for the view that the liquefaction of starch paste is due to a specific enzyme (the so-called amylophosphatase of Waldschmidt-Leitz and Mayer, *Z. physiol. Chem.*, 1935, **236**, 168), which is distinct from both α- and β-amylase and it may indeed be the constituent of saliva which is responsible for the " sensitisation " of dextrin-A.

It is not, however, essential to the argument to distinguish between the amylolytic, liquefying and " sensitising " activities of saliva. We have referred to the enzyme as an α-amylase, but this has been for convenience only and does not commit us to the view that the same enzyme is responsible for all three functions. We confine ourselves to the assumption that saliva contains an enzyme system which is capable of hydrolysing the polymeric linkages of starch and dextrin-A.

K. H. Meyer (*loc. cit.*) finds an explanation of the step-wise degradation of amylopectin by β-amylase in the assumption, for this component of starch, of a highly ramified structure constituted of chains of different length so inter-linked that a single chain may show as many as four branchings (see *Helv. Chim. Acta*, 1940, **23**, 880, Fig. I). It is not possible to attach a quantitative significance to the structure proposed by Meyer and indeed

it is doubtful if the author intended to express thereby any other than a qualitative interpretation of the facts. It must be emphasised, nevertheless, that the weight yields, taken in conjunction with the chain lengths, of dextrins-A and -B are all important. On no system of multiple branching of the Meyer type does it seem possible to account for the formation of as much as 50% by weight of dextrin-A. Furthermore, in such a formulation, the assumption is implicit that the sensitising enzyme, like β-amylase, makes an end-wise attack on the unit chains and that only those polymeric links are hydrolysed which may be approached by the enzyme directly from a free, non-reducing chain termination.

Another explanation is, however, possible and indeed seems to us to be the more probable, inasmuch as it interprets the quantitative, as well as the qualitative, data and does not postulate a needlessly complex and irregular system of multiple branchings for the structure of amylopectin.

The hypothesis which we propose attempts to reconcile the facts of amylolysis with the simple, laminated structure which we regard as best representing the chemical properties of the amylopectin component of starch (I). The hypothesis is dependent upon two assumptions: (1) the " sensitising " enzyme effects the rupture of *all* polymeric links, irrespective of their positions in the laminated structure; (2) the unit chains so liberated are incapable of independent existence for a measurable time and consequently a laminated structure is re-constituted by the re-establishment of polymeric linkages between the unit chains. The probability is very small that the new 1 : 6-linkages between the chains will occupy the same positions relative to the long axes of the chains as they formerly occupied. Kinetic considerations indicate, moreover, that the net effect of the " sensitisation " of dextrin-A (IV) will be a shift in the mean position of the 1 : 6-glucosidic links nearer to the mid-points of the unit chains of dextrin-A (V). This sensitised dextrin-A presents an appropriate substrate for the further action of β-amylase and dextrin-B (VI) is produced thereby.

The unit chain-length of dextrin-B being 7—8, it follows that the mean positions of the re-established polymeric linkages in (V) involve the 7th or 8th glucose residue, counting from the reducing ends of the chains. In terms of averages only, there is in the sensitisation process a displacement of the polymeric linkages from the 11th to the 7th glucose member, counting from the reducing end.

Although the ratio of the unit chain-lengths of dextrin-A and dextrin-B is less than 2 (see Table II), the molecular weight of dextrin-A is five times that of dextrin-B. Clearly dextrin-B is not so highly aggregated as dextrin-A from which it is derived, an observation which lends support to the view that sensitisation implies initial depolymerisation, followed by a reaggregation of the unit chains, the number of polymeric links so established being fewer than the number present before depolymerisation.

It is not proposed at this stage to discuss the formation of the dextrins-C and -D. These are clearly the products of the action of α-amylase, about which much less is known than about β-amylase. It is proposed to continue the investigation of the mechanism of α-amylase activity when circumstances permit.

## Experimental.

*Preparation of α-Amylase from Saliva and β-Amylase from Wheat.*—After the mouth had been rinsed out with water, early morning saliva (30 c.c.) was collected and diluted with twice its volume of water, and the mucin separated in a centrifuge. The supernatant liquid was used as the source of α-amylase in the following experiments and could be preserved by the addition of a crystal of thymol. The aqueous solution contained ionised phosphorus and gave positive ninhydrin and xanthroproteic tests for protein. The preparation contained no β-amylase (negative Wijsmann test) but occasionally contained maltase. A new preparation was always tested for maltase by incubation with 5% maltose solution and if found present, the preparation was discarded. The β-amylase was extracted from ungerminated wheat by the method described previously (J., 1937, 793) and the concentration of enzyme solution used there was employed in the present work.

*The Action of Salivary Amylase, followed by β-Amylase, on α-Amylodextrin (Dextrin-A).*—In each of a series of flasks in a thermostat at 38° were placed 200 c.c. of a 2% aqueous solution of α-amylodextrin (prepared from potato starch by the method of Haworth, Hirst, Kitchen, and Peat, *loc. cit.*) and 5 c.c. of α-amylase solution. After intervals of time varying from a few seconds to 30 minutes the solution was raised quickly to boiling point to destroy the enzyme; after cooling to 38°, β-amylase solution (10 c.c.) was added, and each mixture incubated for 20 hrs. The extent of hydrolysis of the α-amylodextrin was in each case determined by estimation of the reducing power (R.P.) in terms of maltose of the solution after incubation. It was found that, whereas β-amylase alone has no action on α-amylodextrin, the susceptibility of the latter to β-amylase action reappears when the salivary amylase is allowed to act on the dextrin for even the shortest possible time (a few seconds).

Advantage was taken of this effect of α-amylase to continue the hydrolysis of starch by β-amylase beyond the α-amylodextrin stage. α-Amylodextrin (60 g.) was dissolved in boiling water (900 c.c.), cooled to 38°, mixed with salivary amylase solution (50 c.c.), and then immediately raised to boiling again. After boiling for 15 mins., the solution was cooled, mixed with β-amylase solution (500 c.c.), and incubated at 38° for 30 hrs. Thereafter a further quantity of the enzyme solution (250 c.c.) was added, and the incubation continued for 6 hrs.

The solution (1700 c.c.) was poured into alcohol (8 l.), and the dextrin so precipitated collected on a filter, hardened by grinding under absolute alcohol, washed with ether, and dried in a vacuum. This product will be referred to as dextrin-B (yield, 35 g.).

The alcoholic filtrate was evaporated under diminished pressure to a thin syrup, which cyrstallised on keeping. The crystalline material proved to be maltose hydrate (21 g.), $[\alpha]_D^{18°}$ +114·8° ⟶ +129·8° (*c*, 1·66). It gave an osazone, m. p. 200° (Found: N, 10·3. Calc. for $C_{24}H_{32}O_9N_4$: N, 10·8%). The hydrolysis of α-amylodextrin by β-amylase after the momentary action of α-amylase thus yields dextrin-B (58·3%) and maltose (38·3%).

*Properties of Dextrin-B.*—Dextrin-B was a white gritty solid soluble to a slightly opalescent solution in warm water. β-Amylase was without action on it, although further hydrolysis occurred with salivary amylase and malt amylase. The aqueous solution of dextrin-B was quite stable and no evidence of retrogradation was observed. The solution gave a blood-red coloration with iodine. The dextrin had a slight reducing action on Fehling's solution (1 g. ≡ 0·061 g. of maltose); iodine number, 8; $[\alpha]_D^{18°}$ +156·2° in water (*c*, 2·5) and +126·7° in 5% sodium hydroxide solution (*c*, 1·4)

with no mutarotation. The whole of the phosphorus of the original starch was present in dextrin-B (Found : P, 0·58—0·60% as $P_2O_5$).

*The Methylation of Dextrin-B.*—Dextrin-B (15 g.), dissolved in 5% sodium hydroxide solution (300 c.c.), was treated at room temperature with methyl sulphate (200 c.c.) and 30% sodium hydroxide solution in ten portions at intervals of ½ hr.; the mixture was neutralised and evaporated to dryness. The partially methylated product extracted from the dry residue by chloroform was submitted to further methylation. After four methylations, the methylated dextrin was insoluble in boiling water. The methylation was repeated eight times in all and two lots of 15 g. were combined, boiled with fresh changes of water, dissolved in chloroform, and the solution dried (anhydrous magnesium sulphate). This was concentrated to a syrup, the latter dissolved in ether, and the filtrate after removal of a small residue treated with light petroleum. The precipitate, methylated dextrin-B, was dried at 60° in a vacuum for 2 days. It was a glassy solid, fairly soluble in cold water, insoluble in hot, which showed $[\alpha]_D^{18°}$ +185·0° in chloroform (*c*, 2·0) and $\eta_{sp.}^{20°}$ 0·03 (*c*, 0·4%) [Found : OMe, 43·1; P(as $P_2O_5$), 0·40%].

*The Chain-length of Dextrin-B.*—Dry, ash-free, methylated dextrin-B (21·3 g.) was hydrolysed by being boiled for 6 hrs. with 2% methyl-alcoholic hydrogen chloride (300 c.c.). After neutralisation with silver carbonate and filtration, the solution was evaporated, the residue dissolved in ether and filtered, and the solution again evaporated. The dried mixture of glucosides so obtained was distilled into a Widmer flask until the refractive index of the distillate indicated that only trimethyl methylglucoside was distilling. The contents of the Widmer flask were then separated by distillation at 0·1 mm. pressure into the following fractions :

| Fraction. | Weight (g.). | $n_D^{22°}$. | % OMe. | Fraction. | Weight (g.). | $n_D^{22°}$. | % OMe. |
|---|---|---|---|---|---|---|---|
| 1 | 2·298 | 1·4429 | 61·6 | 4 | 0·458 | 1·4552 | 52·8 |
| 2 | 0·914 | 1·4482 | 57·5 | 5 | 6·720 | 1·4569 | 52·3 |
| 3 | 2·465 | 1·4540 | 53·4 | 6 (residue) | 1·960 | 1·4630 | 48·2 |

(Fractions 4 and 5 were partially crystalline.)

From these figures it was estimated that fractions 1, 2, 3, and 4 contained respectively 2·3, 0·54, 0·38, and 0·03 g. of tetramethyl methylglucoside, the total yield of which was thus 15·3% of the weight of methylated dextrin. The value becomes 15·8% after the usual correction is applied, corresponding to a chain length of 7—8 units for the dextrin. The identity of the tetramethyl methylglucoside was established by the conversion of fraction 1 into crystalline 2 : 3 : 4 : 6-tetramethyl glucopyranose, m. p. 88° (alone or in admixture with an authentic specimen); $[\alpha]_D^{20°}$ +102·0° ⟶ +80·0° in water (*c*, 0·5). Similarly fraction 5 was converted into 2 : 3 : 6-trimethyl glucopyranose, m. p. 118°; $[\alpha]_D^{20°}$ +98·0° ⟶ +70·2° in water (*c*, 1·0).

*The Hydrolysis of Dextrin-B by Means of Salivary Amylase.*—Dextrin-B, unlike α-amylodextrin, was not affected by β-amylase after the momentary action on it of α-amylase. It was, however, hydrolysed by the more prolonged action of α-amylase or of malt extract. Dextrin-B (15 g.) in water (250 c.c.) was mixed with saliva solution (50 c.c.) and incubated at 38° for 48 hrs. Thereafter, when the solution was poured into alcohol (2 l.), dextrin-C was precipitated; it was separated in the centrifuge and dried in the manner described for dextrin-B (yield, 10 g.). The alcoholic mother-liquor was concentrated to a thin syrup, which crystallised on keeping. The crystalline material (4 g.) was recognised as maltose hydrate; iodine value, 52; m. p. 108°; $[\alpha]_D^{20°}$ +127·0° (equilibrium value) in water (*c*, 3·0). It formed maltosazone, $[\alpha]_D^{20°}$ +56·4° in methyl alcohol (*c*, 1·2). No glucose could be detected. Thus, by the action of α-amylase on dextrin-B, there are formed dextrin-C (67%) and maltose (27%).

*Properties of Dextrin-C.*—Dextrin-C was a white gritty solid, soluble in cold water to a clear solution which showed no retrogradation on standing. The dextrin reduced Fehling's solution, had iodine value 13, and showed $[\alpha]_D^{17°}$ +147·6° in water (*c*, 1·2) with no mutarotation. The whole of the phosphorus in the original starch was present in the dextrin [Found : P (as $P_2O_5$), 0·98%]. The dextrin gave no colour with iodine and was not further hydrolysed by β-amylase, α-amylase (saliva), malt extract, or taka-diastase, but was slowly attacked by pancreatin.

*The Methylation of Dextrin-C.*—The procedure adopted for the methylation in the cold of dextrin-C was the same as that used for dextrin-B. The product of eight methylations was a brown-white solid, which could not be purified by the usual method, since it was soluble in light petroleum. It contained OMe, 44·5; ash, 0·50; P (as $P_2O_5$), 0·23% and showed $\eta_{sp.}^{20°}$ 0·073 (*c*, 0·8 in *m*-cresol) and $[\alpha]_D^{17°}$ +182·3° in chloroform (*c* 1·3). The methylated dextrin was soluble in ether, alcohol, light petroleum, acetone, chloroform, and was partly soluble in water.

*The Chain-length of Dextrin-C.*—Methylated dextrin-C (11·54 g.) was hydrolysed, and the resulting methylglucoside mixture fractionally distilled as previously described for dextrin-B. The following fractions were obtained :

| Fraction | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Weight (g.) | 1·389 | 0·469 | 0·5765 | 0·853 | 5·054 | 0·606 |
| $n_D^{21·5°}$ | 1·4422 | 1·4440 | 1·4468 | 1·4518 | 1·4582 | 1·4678 |
| % OMe | 61·4 | 60·5 | 59·1 | 55·7 | 52·2 | 44·2 |

(Fraction 5 was crystalline.)

It was estimated that fractions 1, 2, 3, and 4 contained respectively 1·39, 0·41, 0·38, and 0·30 g. of tetramethyl methylglucoside, a total of 2·48 g. from 11·5 g. of methylated dextrin-C. After correction, the yield becomes 22%, corresponding to a chain length of 5—6 units.

Fraction 1, on hydrolysis, gave 2 : 3 : 4 : 6-tetramethyl glucopyranose, m. p. 88°; $[\alpha]_D^{16°}$ +102·2° ⟶ +79·4° in water (*c*, 0·8) (Found : OMe, 52·2. Calc. for $C_{10}H_{20}O_6$ : OMe, 52·6%). Fraction 5 was converted into 2 : 3 : 6-trimethyl glucose, m. p. 118°; $[\alpha]_D^{16°}$ +98·0° ⟶ +70·0° in water (*c*, 1·6) (Found : OMe, 41·5. Calc. for $C_9H_{18}O_6$ : OMe, 41·9%).

*The Action of Pancreatin on Dextrin-C.*—Commercial pancreatin (5 g.), which contained glucose, was purified by shaking with water (30 c.c.), filtering and pouring the filtrate into alcohol (300 c.c.). The flocculent precipitate formed was collected in a centrifuge, washed with alcohol, and dried in a vacuum.

Dextrin-C (1 g.), dissolved in water (4 c.c.), was incubated for 48 hrs. at 38° with purified pancreatin (30 mg.) and a trace of sodium chloride. The solution, which reduced Fehling's solution, was poured into an excess of alcohol. Dextrin-D separated as a flocculent white precipitate, which was purified by reprecipitation, washed with alcohol, acetone and ether, and dried in a vacuum (yield, 0·8 g.). In the aqueous-alcoholic mother-liquors the only sugar detected was maltose.

It was found that a dextrin with identical properties was prepared in this way by the action of commercial pancreatin. In subsequent preparations the purification of the pancreatin was omitted.

*Properties of Dextrin-D.*—The dextrin reduced Fehling's solution, had iodine number 14·2, but gave no colour with iodine. It was easily soluble in cold water, in which it showed $[\alpha]_D^{18°}$ +116·0° (*c*, 0·7). In 5% sodium hydroxide solution it had $[\alpha]_D^{18°}$ +110·9° ⟶ +95·3° in 12 hrs. (*c*, 0·6). The solution in alkali became brown, but this coloration disappeared on exposure to air for several hours. No phosphorus was lost during the hydrolysis (Found : $P_2O_5$, 1·25%).

*The Methylation of Dextrin-D.*—The dextrin (2 g.) was methylated as before by seven treatments with the methylating reagents. After each treatment, the product was extracted with chloroform. Yield, 1 g. The methylated dextrin (OMe, 46·0%) had $[\alpha]_D^{19°}$ +175·6° in chloroform (*c*, 0·4%); ash, 0·24%; $\eta_{sp.}^{20°}$ 0·080 (*c*, 0·8% in *m*-cresol).

*Chain-length of Dextrin-D.*—The methylated dextrin (0·90 g.), hydrolysed under the usual conditions with methyl-alcoholic hydrogen chloride, gave a mixture of methylglucosides (1·03 g.), which was separated by distillation at 0·04—0·07 mm. pressure.

| Fraction | 1 | 2 | 3 | 4 | Residue |
|---|---|---|---|---|---|
| Weight (g.) | 0·235 | 0·227 | 0·111 | 0·056 | 0·24 |
| $n_D^{18°}$ | 1·4462 | 1·4562 | 1·4578 | 1·4600 | — |
| OMe % | 59·9 | 54·0 | 50·8 | 49·0 | 40·1 |

It was estimated that fractions 1 and 2 contained respectively 0·202 and 0·027 g. of tetramethyl methylglucoside. This yield corresponds to a chain-length for dextrin-D of 4·8 units (without correction for loss) or 4·6 units (with correction). Tetramethyl glucose and 2 : 3 : 6-trimethyl glucose were obtained in crystalline form by the hydrolysis of fractions 1 and 3 respectively.

A. E. Hills Laboratories,
The University, Edgbaston, Birmingham, 15.

[*Received, September 11th*, 1943.]

---

## 167. *The Constitution of Yeast Ribonucleic Acid. Part VI. The Nature of the Carbohydrate Radicals.*

By J. Masson Gulland and Geoffrey R. Barker.

*d*-Ribose has come to be regarded as the carbohydrate of yeast nucleic acid and the related nucleotides. Examination of the evidence on which this conclusion is based shows it to be unsatisfactory and the question has been re-examined. *d*-Ribose, and *l*-lyxose in small amount, have been identified, in the form of benziminazole derivatives, in the products of hydrolysis of yeast nucleic acid, and *d*-ribose has been similarly identified as the carbohydrate of guanylic, adenylic and cytidylic acids prepared from yeast nucleic acid, which is therefore designated correctly as the ribonucleic acid of yeast. It is believed that this is the first occasion on which *l*-lyxose has been identified as occurring in a product of natural origin.

It seems now to be usually assumed that the carbohydrate constituent of the pentose nucleotides and polynucleotides is *d*(−)-ribose. Examination of the evidence for this conclusion, however, revealed inconsistencies which made a reinvestigation of the question desirable.

Kossel first reported (*Arch. Anat. Physiol.*, 1891, 181) the presence of carbohydrate in yeast nucleic acid and believed (*ibid.*, 1893, 157) it to consist of a hexose and a pentose. Hammarsten (*Z. physiol. Chem.*, 1894, **19**, 19) and Salkowski (*ibid.*, 1899, **27**, 507) isolated from hydrolysed ox pancreas nucleoprotein a compound thought to be a pentosazone. Neuberg (*Ber.*, 1902, **35**, 1467) obtained from the same source an osazone which he believed to be derived from *d*(+)-xylose.* Attention then turned to the inosic acid of Liebig's extract of meat, of which the sugar was considered to be *d*(+)-xylose by Neuberg and Brahn (*Biochem. Z.*, 1907, **5**, 438), *dl*-arabinose by Bauer (Hofmeister's *Beitrage*, 1907, **10**, 345), and *d*(−)-lyxose by Haiser and Wenzel (*Monatsh.*, 1909, **30**, 147, 377). Levene and Jacobs (*Ber.*, 1909, **42**, 1198) then succeeded in obtaining the crystalline sugar from inosic acid by a two-stage hydrolysis involving the isolation of pure inosine (*Ber.*, 1909, **42**, 335), and later (*ibid.*, p. 3247) concluded that the sugar was *d*(−)-ribose after showing that it gave a *p*-bromophenylosazone which was the optical antipode of *l*-arabinose *p*-bromophenylosazone and on oxidation yielded an optically inactive trihydroxyglutaric acid, thus excluding the possibility of the sugar being *d*-arabinose.

Levene and Jacobs (*Ber.*, 1909, **42**, 2102, 2469, 2474, 2703) also concluded that the sugar was *d*(−)-ribose in the guanylic acids of liver and pancreas, in yeast nucleic acid and in guanosine and adenosine derived from that acid. The evidence, however, was scanty, being either the specific rotation only of the crystalline sugar or the comparison of the melting point and rotation of the osazone with those of an impure sample of the osazone prepared from the sugar of inosic acid. It will be evident that the identification of the sugar in these nucleotides depends largely on the reliability of the designation of the sugar of inosic acid and not on a comparison with an authentic sample of *d*(−)-ribose; at that time such a sample was not available. Moreover, subsequent investigations detract from the value of the determination of specific rotation alone as a reliable method of identification of *d*(−)-ribose, since Phelps, Isbell, and Pigman (*J. Amer. Chem. Soc.*, 1934, **56**, 747) showed that this sugar exhibits a remarkable and rapid mutarotation, in which there is a minimum value, and the initial and the final specific rotation are not greatly different at rather higher than −23°. Levene's published specific rotations for *d*(−)-ribose, varying from −19·2° to −19·5°, lie a little to either side of the mutarotation minimum at −18·8°, and the question of mutarotation does not seem to have been considered by him. Further uncertainty as to the validity of Levene's conclusions arises from the wide discrepancies between the melting points of the phenylhydrazone and the *p*-bromophenylhydrazone obtained from the sugar of inosic acid and the accepted values for these derivatives of ribose quoted by Levene and Jacobs (*Ber.*, 1909, **42**, 2102):

| | Sugar from inosic acid. | Ribose. | Xylose. | Arabinose. |
|---|---|---|---|---|
| Phenylhydrazone | 124—127° | 154—155° | — | 153° |
| *p*-Bromophenylhydrazone | 172—173 | 160 | 128° | 165 |

* Throughout this paper pentoses are designated in accordance with modern nomenclature.

The recognition of the sugar in the pyrimidine nucleotides and nucleosides as *d*(−)-ribose was carried out (i) by simultaneous hydrolysis of the nucleoside and oxidation of the sugar to the aldonic acid (Levene and La Forge, *Ber.*, 1912, **45**, 608), which was identified as *d*-ribonic acid by the melting point of the phenylhydrazide, and (ii) by comparison of the osazone of the sugar, obtained by acid hydrolysis of the nucleoside after catalytic hydrogenation, with the osazone obtained in the earlier work (1909).

In 1909, Rewald (*Ber.*, 1909, **42**, 3134), in knowledge of Levene's results, reported the isolation from pancreas nucleoprotein of a sugar which yielded an osazone identical with that of *d*(+)-xylose.

The descriptions of various preparations of *d*(−)-ribose since the 1909—1912 period (Levene and Tipson, *J. Biol. Chem.*, 1931, **92**, 109; Levene and Stiller, *ibid.*, 1933, **102**, 187; 1934, **106**, 421; Steiger, *Helv. Chim. Acta*, 1936, **19**, 189; Bredereck, *Ber.*, 1938, **71**, 408) mention no physical properties, *e.g.*, crystalline form, melting points, optical rotations, by which the sugar then described could now be identified, or which could be used for comparison with the earlier results. Further the identification of the sugar in the nucleosides crotonoside (Cherbuliez and Bernhard, *Helv. Chim. Acta*, 1932, **15**, 978) and uric acid riboside (Davis, Newton, and Benedict, *J. Biol. Chem.*, 1922, **54**, 595) consisted of a comparison of the melting point and rotation of the sugar from these sources with those of a sample of ribose supplied by Levene. It is clear, therefore, that Levene and his collaborators alone were responsible for the identification of the sugar of the nucleotides as *d*(−)-ribose, whereas other investigators either preferred other alternatives or provided insufficient evidence to enable their agreement with Levene to be assessed. It is always possible, however, that pentoses other than *d*(−)-ribose may have been present, depending on the source of the nucleotides.

This was the position until our work was practically completed. Recently, however, Gurin and Hood (*J. Biol. Chem.*, 1941, **139**, 775) have shown that the carbohydrate of streptococcal nucleic acid is solely or mainly ribose, and v. Euler, Karrer, and Usteri (*Helv. Chim. Acta*, 1942, **25**, 323) and Schlenk (*J. Biol. Chem.*, 1942, **146**, 619) have concluded that the carbohydrate of cozymase is *d*(−)-ribose, in each case using methods different from those now described.

It was evident that independent investigation of the nature of the sugar in pentose nucleic acids and related compounds was required, and it was desirable that the method used should be capable of detecting more than sugar; the theoretical reasons for the latter proviso need not be discussed at present. It was decided to open this series of investigations with a study of yeast nucleic acid and its nucleotides.

Our first experiments were made with 2 : 4-dinitrophenylhydrazine as reagent, but were abandoned because the compounds isolated were osazones instead of the hoped-for hydrazones. Yeast nucleic acid was hydrolysed with 2% sulphuric acid, and a solution of 2 : 4-dinitrophenylhydrazine hydrochloride was added to the solution obtained by removal of the pyrimidine nucleotides, purines and phosphoric acid. The product was fractionated into two portions, melting at 259° (decomp.) and 290—291° (decomp.), both of which had the composition of a pentose 2 : 4-dinitrophenylosazone. By refluxing a solution of 2 : 4-dinitrophenylhydrazine and *d*(−)-arabinose, *arabinose*-2 : 4-*dinitrophenylosazone* was obtained, melting point 259° (decomp.), which was not depressed by admixture with the lower-melting compound obtained from nucleic acid. This was, therefore, the 2 : 4-dinitrophenylosazone of *d*(−)-ribose or *d*(−)-arabinose. The fraction melting at 290—291° obtained from nucleic acid constituted only a small part of the total yield, and it was not possible to establish its constitution. In view of the existence of isomeric derivatives of 2 : 4-dinitrophenylhydrazine (Bredereck, *Ber.*, 1932, **65**, 1833; Bredereck and Fritsche, *Ber.*, 1937, **70**, 802), it could not be assumed that the compound was the 2 : 4-dinitrophenylosazone of xylose or lyxose, and attempts to obtain this derivative from *d*(+)-xylose were unsuccessful.

It was then decided to abandon experiments with dinitrophenylhydrazine and apply the procedure of Moore and Link (*J. Biol. Chem.*, 1940, **133**, 293) whereby the sugar is oxidised to the aldonic acid, which is condensed with *o*-phenylenediamine to give an aldobenziminazole (polyhydroxyalkylbenziminazole). At the time this work was carried out, the properties of *d*-xylo-, *l*-arabo- and *d*-lyxo-benziminazoles had been recorded by Moore and Link, but *d*- and *l*-ribobenziminazoles had not been prepared.

d-*Ribobenziminazole* was therefore made from synthetic *d*-ribonic acid, obtained from calcium *d*-gluconate by Steiger's method (*Helv. Chim. Acta*, 1936, **19**, 189). The properties observed differed widely from those published by Richtmeyer and Hudson (*J. Amer. Chem. Soc.*, 1942, **64**, 1612) subsequently to the completion of our work. In order, therefore, to confirm that our starting material was ribonic acid, the phenylhydrazide was prepared. This compound had the same melting point as that recorded for ribonic phenylhydrazide by Fischer and Piloty (*Ber.*, 1891, **24**, 4214), and depressed the melting point when mixed with the phenylhydrazide of *d*-lyxonic acid which we prepared from *d*-galactose (Kiliani, *Ber.*, 1885, **18**, 1552; Ruff and Ollendorf, *Ber.*, 1900, **33**, 1779; Wohl and List, *Ber.*, 1897, **30**, 3107); the melting points of lyxonic and ribonic phenylhydrazides are the same. Moreover, our *d*-lyxonic acid yielded a benziminazole which had the same melting point as that recorded for this derivative by Moore and Link (*loc. cit.*), and differed widely in properties from our *d*-ribobenziminazole. It was, therefore, concluded that the acid we used was really *d*-ribonic acid, and that our *d*-ribobenziminazole was correctly identified. We are unable to account for the discrepancy between our results and those of Richtmeyer and Hudson.

*l*-Ribobenziminazole was prepared by epimerisation of *l*-arabobenziminazole. This is an example of a method of epimerisation which is more convenient than the normal procedure using the acids, owing to the ease with which the resulting mixture of two benziminazoles may be separated. This method will form the subject of a later communication.

Yeast nucleic acid was hydrolysed with 2% sulphuric acid; this hydrolyses the purine nucleosides to purine, sugar and phosphoric acid, but has little effect on the pyrimidine nucleotides. The syrup remaining after the removal of the pyrimidine nucleotides, purines and phosphoric acid was oxidised and condensed with *o*-phenylenediamine. Two fractions were obtained from the condensation product; the less soluble fraction, the bulk of the product, was identical with synthetic *d*-ribobenziminazole. The more soluble fraction, which was obtained in very small yield, had the same melting point as *d*- and *l*-lyxobenziminazole and was shown to be identical with *l*-lyxobenziminazole; the melting point of a mixture with *d*-lyxobenziminazole was depressed but not that of a mixture with *l*-lyxobenziminazole. The *l*-lyxonic acid required was prepared from *l*-arabinose by oxidation to *l*-arabo-trihydroxyglutaric acid (Kiliani, *Ber.*, 1888, **21**, 3007), of which the monolactone was reduced, following the method of Fischer and Herz (*Ber.*, 1892, **25**, 1249), to a mixture of *l*-arabonic and *l*-lyxonic acids, which were separated as the benziminazoles.

Cytidylic, guanylic and adenylic acids derived from yeast nucleic acid all yielded only *d*-ribobenziminazole after simultaneous hydrolysis and oxidation by a mixture of bromine and hydrobromic acid.

The results described above show that *d*(−)-ribose is to be regarded as the chief carbohydrate constituent of yeast nucleic acid, which is therefore correctly designated as the ribonucleic acid of yeast. Levene's conclusions are therefore confirmed. *l*-Lyxose was present to a small extent as a subsidiary sugar in the commercial sample examined. As far as is known, this is the first record of the detection of *l*-lyxose in naturally occurring material.

The examination of the sugar of nucleotides and polynucleotides from other sources is being undertaken.

## Experimental.

*Isolation of* d-*Ribo- and* l-*Lyxo-benziminazoles from Yeast Nucleic Acid.*—Yeast nucleic acid (B.D.H.) (100 g.) was refluxed with 2% sulphuric acid (1 l.) for 2 hours, and after removal of the guanine sulphate from the resulting solution, cytidylic and uridylic acids were removed by Bredereck and Richter's method (*Ber.*, 1938, **71**, 718). The resulting sugar solution, free from other organic nucleic acid constituents, was concentrated under reduced pressure to about 50 c.c., made alkaline with excess of hot saturated baryta, filtered to remove barium phosphate and brucine, and finally freed from brucine by repeated extraction with chloroform. Barium ions were exactly removed with dilute sulphuric acid, and the barium sulphate was centrifuged and washed with water until free from pentose-containing material. The combined centrifugate and washings contained 2 g. of pentose (8·6% of the purine nucleotide pentose in the nucleic acid used) when analysed by Hinton and Macara's method (*Analyst*, 1924, **49**, 2). The solution was evaporated under reduced pressure to a thick syrup, which was oxidised by Moore and Link's method (*loc. cit.*). The resultant potassium aldonate (A, see below) was collected and condensed with *o*-phenylenediamine by Moore and Link's method, and the product crystallised from water. *d*-Ribobenziminazole separated in rosettes of fine needles, m. p. 239° (decomp.), not depressed by the benziminazole from synthetic *d*-ribonic acid.

Ammoniacal cupric acetate was added to the filtrate from the ribobenziminazole until no further precipitate formed. The solid was collected, washed with water, suspended in water (5 c.c.), and decomposed with hydrogen sulphide. The solution was filtered from copper sulphide, and evaporated under reduced pressure at room temperature over phosphoric oxide. A small quantity of *l*-lyxobenziminazole separated, and after crystallisation from water formed needles, m. p. 189·5°, not depressed by synthetic *l*-lyxobenziminazole, m. p. 189°, but depressed to 178° by *d*-lyxobenziminazole, m. p. 189°.

When barium iodide in dry methyl alcohol was added to the filtrate from the potassium aldonate (see A above), a small precipitate was obtained, but this yielded no benziminazole on condensation with *o*-phenylenediamine either at 130—140° or at 180° (cf. Moore and Link, *loc. cit.*). This excludes the presence of aldonic acids other than ribonic and lyxonic.

d-*Ribobenziminazole.*—(i) *From guanylic acid.* A mixture of guanylic acid (4 g.), prepared from B.D.H. yeast nucleic acid by Jones and Perkins' method (*J. Biol. Chem.*, 1924—5, **62**, 557), and N-hydrobromic acid (100 c.c.) was refluxed for 2 hours, during which period bromine (60 g.) was added in four batches, and then shaken at room temperature for 8 hours. After the excess of bromine had been removed by distillation, the hydrogen bromide was largely removed by the addition of lead carbonate to the hot solution, thorough cooling, and filtration from lead bromide. Excess of lead was removed by precipitation with hydrogen sulphide, and the remainder of the bromide ions by grinding the filtrate from the lead sulphide with freshly prepared silver oxide, after it had been freed from hydrogen sulphide. The solution was filtered and, after removal of silver ions by precipitation with hydrogen sulphide, the filtrate from silver sulphide was evaporated under reduced pressure to a thick syrup, in which the content of aldonic acid was determined by titrating an aliquot portion (about 20 mg.) with N/100-sodium hydroxide, with phenolphthalein as indicator. The main portion of the syrup (0·57 g. of aldonic acid) was heated at 130—140° for 2 hours with *o*-phenylenediamine (0·48 g.), glacial phosphoric acid (0·37 c.c.), concentrated hydrochloric acid (0·37 c.c.), and diethylene glycol (1·36 c.c.) (compare Lomar, Dimler, Moore, and Link, *J. Biol. Chem.*, 1942, **143**, 552). The resulting syrup was dissolved in water (2 c.c.), and the solution decolorised with charcoal and made just alkaline to litmus by addition of aqueous ammonia (*d* 0·880). Needles began to form immediately, and after being cooled thoroughly, were collected, washed successively with water, alcohol and ether, and dried. *d*-Ribobenziminazole had m. p. 239—240°, not depressed by a sample prepared from *d*-ribonic acid. Second and third crops of ribobenziminazole were obtained by concentration of the mother-liquors, but no other product could be isolated.

(ii) *From yeast adenylic acid.* A mixture of adenylic acid (2 g.), prepared from B.D.H. yeast nucleic acid by Jones and Perkins' method (*loc. cit.*), N-hydrobromic acid (50 c.c.), and bromine (10 c.c.) was shaken at room temperature for 48 hours, a further quantity of bromine (5 c.c.) being added after 24 hours. The mixture was refluxed for 2 hours to complete the reaction. The resulting solution was freed from bromine and hydrogen bromide as described above and concentrated to a thick syrup under reduced pressure. After titration of an aliquot part with N/100-sodium hydroxide, the syrup (0·12 g. of aldonic acid) was heated for 2 hours at 130—140° with *o*-phenylenediamine (0·1 g.), concentrated hydrochloric acid (0·08 c.c.), glacial phosphoric acid (0·08 c.c.), and diethylene glycol (0·3 c.c.). The product, when worked up as already described, yielded 0·05 g. of *d*-ribobenziminazole, m. p. 239°, identical with a sample prepared from *d*-ribonic acid. No other compound could be isolated from the reaction.

(iii) *From cytidylic acid.* A mixture of cytidylic acid (2·7 g.), prepared from B.D.H. yeast nucleic acid by Bredereck's method (*Ber.*, 1938, **71**, 718), N-hydrobromic acid (100 c.c.), and bromine (14 c.c.), was refluxed for 8·5 hours and shaken at room temperature for 48 hours. After the solution had been freed from bromine and hydrobromic acid and its aldonic acid content determined as before, condensation was carried out at 130—140° for 2 hours with *o*-phenylenediamine

(0·14 g.), concentrated hydrochloric acid (0·11 c.c.), glacial phosphoric acid (0·11 c.c.), and diethylene glycol (0·4 c.c.). The product was worked up as already described, and *d*-ribobenziminazole, m. p. 239—240°, was obtained identical with that obtained from *d*-ribonic acid.

A careful examination of the mother-liquors for other benziminazoles or for aldonic acids not undergoing condensation at 130—140° (*e.g.*, xylonic acid) showed that these compounds were absent.

(iv) *From synthetic* d-*ribonic acid.* Barium *d*-ribonate (1·6 g.), prepared from calcium gluconate by Steiger's method (*Helv. Chim. Acta*, 1936, **19**, 189), was dissolved in water (5 c.c.) and freed from barium ions exactly with sulphuric acid. The solution, to which hydrochloric acid (0·8 c.c.) had been added, was evaporated under reduced pressure to a syrup, which was heated with *o*-phenylenediamine (0·7 g.) and glacial phosphoric acid (0·5 c.c.) for 2 hours at 130—140°. The product was dissolved in water (5 c.c.), and the solution decolorised with charcoal and diluted to 15 c.c. with water. After the solution had been cooled in running water, a small quantity of non-nitrogenous material was removed; the filtrate, on standing, yielded d-*ribobenziminazole* as rosettes of fine needles, m. p. 239—240°, after being washed successively with water, alcohol, and ether (Found : N, 11·6. $C_{11}H_{14}O_4N_2$ requires N, 11·8%). The m. p. was not altered by further recrystallisation from water. In 5% aqueous citric acid ($c$ = 1·19), $[\alpha]_D^{20°}$ was −50·4°. Richtmeyer and Hudson (*loc. cit.*) record that their product formed prismatic needles, m. p. about 190° (decomp.), with $[\alpha]_D^{20°}$ +21·6 ($c$ = 2·0).

The picrate crystallised from water in long yellow needles, m. p. 179—180°.

It is convenient to state here that in our preparations of benziminazoles from pentose aldonic acids, we have observed that the more soluble members of the group are liable to be contaminated with ammonium phosphate (from the reaction mixture), which melts at approximately 187°.

*d-Ribonic Phenylhydrazide.*—(i) *From synthetic* d-*ribonic acid.* Barium ions were removed exactly with sulphuric acid from a solution of synthetic barium *d*-ribonate (0·3 g.) in water (5 c.c.). The filtrate was evaporated under reduced pressure to a syrup, which was heated with phenylhydrazine (0·1 c.c.) for 2 hours at 100°. The phenylhydrazide, crystallised three times from industrial methylated spirit, formed long fine needles, m. p. 163° (Found : N, 11·1. Calc. for $C_{11}H_{16}O_5N_2$ : N, 10·9%). Fischer and Piloty (*loc. cit.*) give m. p. 162—164°.

(ii) *From guanosine.* A mixture of guanosine (56 mg.), 2% hydrobromic acid (10 c.c.), and bromine (0·5 c.c.) was refluxed for 3 hours, and the solution freed from bromine and hydrobromic acid as previously described; after removal of the bromine, guanine hydrobromide separated and was removed. The syrup, obtained by evaporating the final solution under reduced pressure, was condensed with phenylhydrazine (0·1 c.c.) as described above; the phenylhydrazide had m. p. 163° (Found : N, 10·9%), not depressed by the phenylhydrazide from synthetic *d*-ribonic acid.

d-*Lyxonic Phenylhydrazide and* d-*Lyxobenziminazole.*—*d*-Lyxonic acid was prepared by oxidation of *d*-galactose with bromine (Kiliani, *Ber.*, 1885, **18**, 1552), degradation of the calcium *d*-galactonate thus obtained with hydrogen peroxide in presence of ferric acetate (Ruff and Ollendorf, *Ber.*, 1900, **33**, 1798), and oxidation of the resulting syrupy *d*-lyxose by Moore and Link's method (*loc. cit.*).

Condensation with phenylhydrazine as already described (Fischer and Bromberg, *Ber.*, 1896, **29**, 581) yielded the phenylhydrazide in fine needles, m. p. 162—163° (Found : N, 10·9. Calc. for $C_{11}H_{16}O_5N_2$ : N, 10·9%). A mixture of this phenylhydrazide with that of *d*-ribonic acid melted at 148—152°.

Condensation of *d*-lyxonic acid with *o*-phenylenediamine by the standard procedure yielded *d*-lyxobenziminazole, m. p. 189°, as described by Moore and Link.

l-*Lyxobenziminazole.*—*l*-Arabinose (2·5 g.) was oxidised to *l*-arabo-trihydroxyglutaric acid with nitric acid (Ruff, *Ber.*, 1899, **32**, 558), and the syrupy acid thus obtained was converted into the lactone by being heated at 100° under reduced pressure for 1·5 hours. The lactone was reduced by sodium amalgam in faintly acid (sulphuric) solution (Fischer and Bromberg, *Ber.*, 1896, **29**, 584) until the reducing power of the solution, measured by Folin and Wu's method (*J. Biol. Chem.*, 1920, **41**, 367), fell to a minimum value after its initial rise; this indicated that the aldehyde group formed by reduction of the monolactone had undergone further reduction to a primary alcoholic group. After removal of the mercury, sodium sulphate and sulphuric acid, the solution was evaporated to a syrup, which was condensed with *o*-phenylenediamine in the usual way. The aqueous solution of the product was evaporated in a vacuum desiccator and three crops of needles were collected. The first two consisted of pure *l*-lyxobenziminazole, which formed fine needles, m. p. 189°, the third needed one crystallisation from water to reach this purity owing to contamination with ammonium phosphate. This compound will be described in more detail in a later paper.

*Epimerisation of* l-*Arabobenziminazole.*—A solution of *l*-arabobenziminazole (0·2 g.), prepared from *l*-arabinose (Moore and Link, *loc. cit.*), in water (5 c.c.) containing 10% of pyridine was refluxed for 48 hours. After cooling, the pyridine was removed by distillation under reduced pressure and the solution was cooled, filtered from a slight impurity, and diluted to 50 c.c. Unchanged *l*-arabobenziminazole separated in needles, m. p. 234—235°. The filtrate was evaporated to 15 c.c. and, on cooling, deposited *l*-ribobenziminazole in rosettes of fine needles, m. p. 239°. A mixture with *d*-ribobenziminazole had m. p. 228°.

*Isolation of* 2 : 4-*Dinitrophenylosazones from Yeast Nucleic Acid.*—Yeast nucleic acid (B.D.H.) (100 g.) was hydrolysed as described above in the isolation of ribo- and lyxo-benziminazoles, and the sugar solution, after removal of the other fission products of the nucleic acid and of brucine as before, was mixed with a solution of 2 : 4-dinitrophenylhydrazine (0·3% in 2N-hydrochloric acid) (2 l.). A precipitate formed slowly and was collected at intervals of several days. After several weeks, the combined precipitates were dissolved in the minimum quantity of pyridine, and water was added until a precipitate formed, which was redissolved by warming. On cooling, a mixture of long fine needles and very small, hexagonal plates separated. The needles were obtained free from hexagonal plates by filtration through a coarse filter paper (Whatman No. 1) and the hexagonal plates were collected by filtration through a fine filter paper (Whatman No. 42). The needles were recrystallised three times from dry pyridine and formed brilliant red rhombs, m. p. 259° (decomp.) (Found : C, 40·0; H, 3·3; N, 22·4. $C_{17}H_{16}O_{11}N_8$ requires C, 40·1; H, 3·1; N, 22·05%). The hexagonal plates, after three crystallisations from dry pyridine, formed an orange microcrystalline powder, m. p. 290—291° (Found : C, 40·9; H, 3·1. $C_{17}H_{16}O_{11}N_8$ requires C, 40·1; H, 3·1%).

d(−)-*Arabinose*-2 : 4-*dinitrophenylosazone.*—A mixture of *d*(−)-arabinose (0·5 g.), dissolved in water (5 c.c.), and 2 : 4-dinitrophenylhydrazine (2 g.), dissolved in 50% ethyl alcohol–glacial acetic acid, was refluxed for 1·5 hours. After cooling, the solution was evaporated under reduced pressure to 50 c.c., diluted with water (100 c.c.), and cooled to 0°. The dark red *osazone* which separated was collected and after crystallisation three times from dry pyridine formed brilliant red rhombs, m. p. 259—260° (Found : N, 21·7. $C_{17}H_{16}O_{11}N_8$ requires N, 22·1%), not depressed by the 2 : 4-dinitrophenylosazone of the same m. p. obtained from yeast nucleic acid.

We are indebted to Mr. C. H. Rigby for the preparation of barium *d*-ribonate from calcium gluconate and to Mr. J. E. Still for micro-analyses. It is a pleasure to record the help given by Imperial Chemical Industries Ltd. in the form of grants for chemicals and apparatus.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, September 17th*, 1943.]

# *Recent Advances in the Theory of Reaction Kinetics in Solution.*

TILDEN LECTURE, DELIVERED BEFORE THE CHEMICAL SOCIETY ON DECEMBER 17TH, 1942.

By R. P. BELL.

A LARGE part of the work which has been done on reaction velocities in solution has been concerned with the use of kinetic measurements for obtaining information about the physical or chemical constitution of solutions, or the mechanism of reactions. For example, the evidence for the classical theory of electrolytic dissociation depended to a considerable extent on measurements of the velocity of hydrolysis of esters and the inversion of cane sugar, and more modern views on the nature of electrolyte solutions have received valuable support from the work of Brönsted and his school on reaction kinetics in solution. From a rather different point of view, measurements of kinetic order have often been used to tell us something about the consecutive steps of complicated reactions, only one of which normally determines the observed velocity. In recent years this kind of analysis has proved very fruitful in the hands of Ingold and his collaborators for investigating the mechanism of many of the reactions of organic chemistry, especially in relation to modern electronic theory.

In all these cases the reaction velocities are used primarily as a tool for obtaining useful information, and until fairly recently few workers in this field attempted to develop a theory which would account for the absolute values of the observed velocities for different reactions and different solvents. As has been recently pointed out by Polanyi,[1] indifference to this aspect of the subject seems to have been almost deliberate in some quarters. However, during the last ten years there has been a determined attack on the fundamental problems of reaction velocities in solution, both on the theoretical and on the experimental side. In this lecture I shall try to show how far this attack has succeeded.

For a long time the theoretical approach was confined almost entirely to gas reactions, which was understandable in view of the successes of the kinetic theory of gases, and the failure of attempts to account for the properties of liquids along similar lines. The reason for modern departures from this conservative attitude was originally probably an experimental one, as it was soon found that the simplicity of gas reactions was more apparent on paper than in the laboratory. Very few gas reactions are wholly free from both chain reactions and surface reactions, and even in the absence of these complications it is often found that the kinetic order of the reaction is not a simple integral one, but varies, for example, between the first and the second order. In solution, on the other hand, surface and chain reactions are very rare, and almost all reactions follow accurately either first- or second-order kinetics, unless there are chemical reasons for departures.

On the theoretical side, the fear of complications in solution has rested to some extent on misapprehensions. Although our general knowledge of the liquid state is still very incomplete, many of the difficulties involved are irrelevant when dealing with reactions between solute molecules in fairly dilute solutions. In this there is a close analogy with the thermodynamic properties of solutions, where the behaviour of solutes is frequently just as simple as that of gases at comparable concentrations, even in solvents such as water which themselves exhibit complex properties. Modern theories of solution have concentrated particularly on deviations from such simple behaviour, and the success of some of these theories (notably the Debye–Hückel treatment of electrolytes) may have resulted in a tendency to ascribe too great an importance to such deviations in general. Moreover, the use of reactants showing abnormal thermodynamic behaviour by no means always entails corresponding kinetic complications. For example, in reactions between an ion and a neutral molecule the simple kinetic law of mass action is obeyed up to concentrations where the thermodynamic behaviour of electrolytes is far from ideal.[2] The same state of affairs occurs in reactions between non-electrolytes: thus the reaction between acetic anhydride and ethyl alcohol in benzene solution is a simple bimolecular reaction over a concentration range in which the apparent degree of association of the alcohol (derived from freezing-point measurements) doubles itself.[3] Only in reactions between ions are deviations from simple kinetic behaviour of primary importance, and even in this case they can be largely avoided by working in very dilute solution, or by maintaining a high and constant salt concentration. The high accuracy and reproducibility of kinetic measurements in solution has made it possible to investigate special phenomena such as salt effects, and consecutive or reversible reactions showing complicated kinetics, a circumstance which may sometimes have obscured the large amount of simple kinetic material available for theoretical interpretation.

Before dealing with the different methods of theoretical approach, it is convenient to summarise the experimental material which has to be accounted for.[4] I shall deal only with second-order reactions, since it is only in this case that significant progress has been made. All theoretical treatments involve the temperature dependence of the reaction velocity, and almost all the experimental data have been analysed in terms of the simple Arrhenius equation

$$k_2 = Ae^{-E/RT}$$

where $k_2$ is the bimolecular velocity constant, $E$ the activation energy, and $A$ the collision factor. $E$ has the dimensions of energy, and is usually expressed in kilogram-calories per gram-molecule. $A$ has the same dimensions as $k_2$, *i.e.*, (concentration)$^{-1}$ (time)$^{-1}$, and different authors express it in different units. We shall take the concentration in moles per litre and the time in seconds. In using the above equation it is commonly assumed that both $A$ and $E$ are independent of temperature, and we shall see later that this is only true as a first approximation. However, theory indicates that it is likely to be a fairly good approximation, and this is

borne out by the experimental data, which are rarely sufficiently accurate to detect any temperature variation of these quantities. The simple assumption is certainly adequate for the broad generalisations which will form the chief subject of this lecture.

The experimental values of $E$ cover a wide range (about 7—40 kg.-cals./mole), and do not show any general correlation with the type of reaction or solvent. More theoretical interest attaches to the absolute value of the constant $A$. The data do not at first sight appear to encourage any generalisations, since in the units which we have chosen $A$ varies over the range $10^2$—$10^{19}$: moreover, the values do not, as was at one time supposed, fall into a few narrow categories, but are distributed over the whole range. However, when reactions are divided into classes, the following rough generalisations emerge:

*Reactions between two uncharged molecules.* (*a*) Most organic reactions have $A = 10^5$—$10^7$, with considerable variations from one solvent to another. (*b*) A few reactions involving non-polar reactants and products have $A = 10^7$—$10^{11}$, independent of the solvent.

*Reactions between an ion and an uncharged molecule.* (*c*) Most reactions of this class have $A = 10^9$—$10^{11}$, varying little with the solvent.

*Reactions between two ions.* (*d*) For ions of opposite charge, $A = 10^{13}$—$10^{19}$. For ions of like charge $A = 10^2$—$10^8$. In each case the deviation from $A = 10^{11}$ increases with increasing valency of the reacting ions.

The reactions under (*a*) include those of organic halides with bases to give salt-like products (*e.g.*, the Menschutkin reaction), substitution in aromatic compounds by uncharged reagents, and catalysis by uncharged acids and bases. Class (*b*) includes the small number of reactions which have been studied both in the gas phase and in solution, *e.g.*, polymerisation reactions of unsaturated hydrocarbons, and a few typical gas reactions like the decomposition of ozone and chlorine monoxide.[5] Class (*c*) includes the large number of reactions in which an organic halide reacts with an anion in solution, and also the many reactions catalysed by hydrogen or hydroxyl ions, or other charged acids and bases. Almost all the reactions for which data are available fall into one of the above classes.

There are two types of theoretical treatment which have been used to explain the values of $A$ summarised in the above table, and although their essential unity is gradually becoming more apparent, it is still convenient to treat them separately.[6] In the simple form of the *collision theory* the velocity expression is written in the form

$$k_2 = PZe^{-E/RT}$$

$Z$ is the kinetic theory collision number arrived at by assigning definite radii to the reacting molecules: in the units we have chosen it will always be of the order of magnitude $10^{11}$ at ordinary experimental temperatures. The Boltzmann factor $e^{-E/RT}$ gives the fraction of colliding pairs which will possess sufficient energy to lead to reaction, and $P$ is the factor expressing the probability that other conditions (such as the favourable orientation of the colliding molecules) will be fulfilled. In the *transition state theory* attention is focused on the state of lowest probability through which a pair of molecules pass during the process of reaction, and this state, X, is termed the transition state or the critical complex. It is then possible to express the reaction velocity in terms of the equilibrium constant $K$ for the equilibrium $A + B \rightleftharpoons X$. The expression for the bimolecular velocity constant $k_2$ is

$$k_2 = \tfrac{1}{2}Kv$$

where $v$ is a thermal velocity which will not vary greatly from one reaction to another. (Other apparently different formulations are possible, but are equivalent to the above equation.) $K$ is formally related to the free energy of activation $F$ by the equation $RT \log K = F$, and if $F$ is split up into an energy and an entropy term by the usual equation $F = E - TS$, the equation for the velocity becomes

$$k_2 = \tfrac{1}{2}ve^{+S/R}e^{-E/RT}$$

$v$ and $S$ can be calculated in principle by the methods of statistical mechanics, though the information needed for this calculation is equivalent to that needed to predict $P$ and $Z$, and is not available in our present state of knowledge. The derivation of all the above equations indicates that $P$, $Z$, $v$, and $S$ will all vary only slowly with the temperature, thus agreeing to a first approximation with the simple Arrhenius equation. On the other hand, some caution is necessary in identifying values of $A$ and $E$ obtained by applying the Arrhenius equation to experimental data with those occurring in more exact expressions, since barely detectable deviations from the Arrhenius equation may cause considerable discrepancies between the two sets of values.[7]

Much has been written recently about the comparative status and usefulness of these two theories, and I shall make no attempt to go into the question here, especially as the controversial element in these discussions has largely disappeared. It may, however, be of interest to mention my own attitude as far as practical procedure is concerned. In attempting to account qualitatively for a new kinetic phenomenon I should think first along the lines of the collision theory, but having found a possible explanation I should check it by considering the same problem in the light of the transition state theory. Moreover, if and when data became available for a quantitative treatment, I should use the equations of the transition state theory. However, at present a semi-quantitative treatment is the most which can be attempted, and the use of both methods will be illustrated in the following discussion.

The meagre experimental data for homogeneous bimolecular gas reactions give values of $A = 10^9$—$10^{11}$ for simple molecules, falling to $10^7$—$10^8$ for a few reactions between complex molecules. From the point of

view of the collision theory this corresponds to $P$ values of $10^{-2}$—1 for simple molecules and $10^{-4}$—$10^{-3}$ for complex ones, values which are quite plausible from a geometrical point of view. If the reaction takes place in solution instead of in the gas, the position will be modified to some extent by the interaction between the solvent and the reacting system, which will be at a minimum when the reacting molecules and the transition state are both of low polarity. In this case the effect of the solvent may be pictured merely as a kind of physical interference, and the value of $P$ will be the same in solution as in the gas phase. On the other hand, the collision number $Z$ should be somewhat greater in solution than in the gas, since the free space between the solvent molecules is less than the total volume of the solution. An exact evaluation of this free space factor would demand a much more exact knowledge of the structure of liquids than we yet possess, but various idealised models indicate that $Z$ should be increased by a factor not exceeding 4.[8]

This conclusion agrees with experiment for the class of reactions (*b*) above, where the range of $A$ values, $10^7$—$10^{11}$, is the same as for the bimolecular gas reactions. In these reactions not only are the reactants of low polarity, but the probable mechanisms involve only the making and breaking of homopolar bonds, without any considerable separation of charge at any stage. Direct comparison of $A$ values in the gas phase and in solution has rarely been possible, and the only data of any accuracy are those of Wassermann [9] on the dimerisation of *cyclo*pentadiene in the gas phase and 8 different solvents. The values of $A$ were identical within the experimental error, *i.e.*, they did not differ by a factor of more than 3. Further interesting evidence is obtained from the conversion of para- into ortho-hydrogen, catalysed by oxygen or nitric oxide.[10] This catalysis is not chemical in nature, but depends on the paramagnetic properties of the oxygen or nitric oxide molecules. Only a small fraction of the collisions between the para-hydrogen and the paramagnetic molecules result in conversion, but this fraction is independent of temperature (*i.e.*, does not involve an energy of activation) and would be expected theoretically to be unaffected by the presence of the solvent. Experiment shows that the conversion takes place 1·2—2 times as fast in aqueous solution as in the gas phase, from which it can be safely concluded that the collision numbers on the two phases are in approximately the same ratio.

The transition state theory arrives at the same result for reactants of low polarity, though by an apparently less direct route. For gas reactions, if the two reactants A and B are pictured as structureless spheres of known radii, statistical mechanics can be used to calculate the entropy change in forming the complex X. When this is substituted in the equation for the reaction velocity the resulting expression is identical with that of the collision theory, if $P$ is put equal to 1. When the actual structure of the colliding molecules is taken into account it is still possible to write down the expressions for $S$ and $v$, but they now contain a number of distances and frequencies which can only be estimated roughly. However, the formation of X from complex molecules A and B will always involve the conversion of some rotational degrees of freedom into vibrational ones, and it can be shown that this circumstance will make the term $e^{+S/R}$ smaller than it is for the idealised spherical molecules. This reduction may amount to several powers of 10, and will appear in the factor $A$ of the Arrhenius equation, thus agreeing with the experimental results for complex molecules in the gas phase.[11] Just as in the collision theory, the effect of the solvent can be calculated from first principles only by making simplifying assumptions about the structure of the solvent. If the only effect of the solvent is to reduce the space available to a fraction $\sigma$ of the whole volume, this will increase the entropy change $S$ by an added term $-R \log \sigma$, since in the reaction $A + B \longrightarrow X$ the number of molecules decreases by one. $v$ will be unaffected by the presence of the solvent, so that the collision factor $\frac{1}{2}ve^{+S/R}$ is increased by a factor $\sigma$, just as before. There is also an alternative procedure, which does not make use of any model of the liquid state, but estimates the effect of the solvent upon $S$ from experimental data on the entropy of solution of non-polar molecules in general.[12] This method, when correctly applied,[12] predicts that the factor $A$ will be 2—3 times greater in solution than in the gas, in excellent agreement with the conclusions already reached.

The interaction between solvent and solute is often too intimate to be described in terms of a free-space factor, and this is particularly so in the case of ions. Apart from the possibility of chemical solvation, the powerful electrostatic field will tend to orient solvent molecules round the ion, and this may be expected to modify the simple behaviour described above. It therefore seems at first sight surprising that reactions between an ion and an uncharged molecule [class (*c*) above] have $A = 10^9$—$10^{11}$, *i.e.*, the same as for a bimolecular gas reaction between simple molecules. However, it is important to realise that the significant factor in determining the reaction velocity is not the actual extent of the solute–solvent interaction, but the extent to which this interaction changes when the two reactants collide to form the transition state. If one of the reactants is charged and the other uncharged, the reacting system will have the same net charge throughout the process of forming the transition state, and to a first approximation there will be no change in solvation. The solvent thus plays no direct part in the collision process, and contributes nothing to the entropy change in the process $A^+ + B \longrightarrow X^+$. Hence according to both collision theory and transition state theory the collision factor should be little affected by the solvent, as is found experimentally.

There are, however, many cases in which the reaction process involves a change in the extent of solvation, and it is in fact changes of this kind which are usually invoked to explain all the major differences between gas and solution kinetics.[14] As an example we may consider the reaction between two ions of opposite charges, $A^+$ and $B^-$. Before reaction, both ions will be solvated, but when they come together the collision complex formed will have zero net charge, and will therefore be solvated to a much smaller extent. In this case, therefore, the formation of the transition state involves the de-solvation of a number of solvent molecules, and it is necessary to include these solvent molecules in any theoretical considerations about the reaction

velocity. From the point of view of the transition state theory this means that the equilibrium to be considered is not simply $A^+ + B^- \rightleftharpoons X$, but $AS_m^+ + BS_n^- \rightleftharpoons X + (m + n)S$, where S is a solvent molecule. When a solvent molecule becomes detached from the ion, it exchanges vibrational and librational movement for translation and rotation, and passes from a state of comparative order into one of comparative disorder. This decrease of order is accompanied by an increase of entropy, and the effect of the solvent is thus to make the term $e^{+S/R}$ greater than it would be in the absence of solvent. This agrees with the experimental finding that reactions between oppositely charged ions have $A$ greater than $10^{11}$.

Statistical mechanics gives expressions for the entropy of desolvation, which could be evaluated if the distances and force constants of the solvated ion were known, as well as the structure of the solvent. Although this is not possible, the observed values of $A$ up to $10^{19}$ can be accounted for on the basis of plausible assumptions. It should be pointed out that the increase of entropy associated with desolvation can easily be understood qualitatively without recourse to a detailed treatment. The energy levels predicted by the quantum theory for a molecular vibration are fairly far apart, whereas for rotation they are considerably closer together, and for translation they are so close together that they cannot be directly detected. A change in which vibrations are converted into rotation and translation therefore produces a large increase in the number of energy levels which are available within a given energy range, and thus increases the probability (or entropy) of the system. The simplest application of this principle is, of course, in the equilibrium between a diatomic molecule and free atoms, $A_2 \rightleftharpoons 2A$, where one degree of freedom of vibration and two of rotation are converted into three translational degrees of freedom. For this reason the ratio (atoms)/(molecules) is much greater than the Boltzmann factor $e^{-Q/RT}$; *i.e.*, the dissociation into atoms is accompanied by an increase of entropy.

It would seem at first sight that the collision theory could never account for values of $A$ considerably greater than $10^{11}$, since if the factor $P$ is taken to represent additional restrictions due to orientation, it must be less than unity. However, the actual collision which takes place is between two unsolvated ions, and not between the original solvated reactants. In order to calculate the number of these collisions it is necessary to consider first the equilibrium between solvated and unsolvated ions, where the effect of the entropy change will again be apparent.

It is also possible for the formation of the transition state to be accompanied by an *increase* of solvation, and this is the case for a large number of reactions between unchanged molecules. In many of these the products of reaction are ionic, for example in the Menschutkin reaction $R_3N + RI \longrightarrow [R_4N]^+[I]^-$, and many analogous reactions between an organic base and a halogen compound. The transition state in these reactions, although not bearing any net charge, is likely to involve a considerable separation of charge, with the production of a dipole. It will therefore have a more powerful external field than the reacting molecules separately, and will orient more solvent molecules. The low values of $A$ observed for this type of reaction are undoubtedly connected with this increase of solvation.[15] From the point of view of the transition state theory the problem is just the converse of that mentioned above: conversion of rotation and translation into vibration involves an increase of order, a decrease of entropy, and hence a low value for $e^{+S/R}$. In the collision picture the act of reaction involves not only the collision and orientation of the two reactant molecules, but also the simultaneous presence and orientation of a number of solvent molecules, which naturally reduces the steric factor $P$.

When two uncharged molecules react, the formation of a transition state of high polarity is not confined to those reactions in which the final products are ions. A large proportion of the reactions of organic chemistry are now believed to take place by an ionic mechanism; *i.e.*, the electronic displacements involved in the reaction process resemble those which would lead to the formation of ions, though actual free ions need not be formed either as final products or at any intermediate stage.[16] These reactions will have a transition state of higher polarity than the initial reactants, and low values of $A$ are to be expected. This is in fact the case for the great majority of reactions between uncharged molecules [group (*a*) above], most of the exceptions being the few " typical gas reactions " already mentioned, where the reaction mechanism is not believed to be ionic. An interesting single exception is the reaction of lead tetra-acetate with glycols, where an $A$ value of approximately $10^{11}$ is coupled with independent evidence that the reaction mechanism involves free radicals rather than ions.[17]

Since the orientation of solvent round the polar transition state constitutes an unfavourable factor for the completion of the reaction, it might be asked why reactions of this type do not take place without the occurrence of solvation, thus removing the reasons for a low value of $A$. However, the co-operation of the solvent affects not only the value of $A$, but also the value of $E$, and in the present case the orientation of the solvent decreases the energy necessary to produce the charge separation in the critical complex. The effect of solvation is therefore to decrease $A$ but to increase $e^{-E/RT}$, and in practice the latter effect usually appears to be the greater, thus favouring the reaction mechanism involving solvation. Correspondingly it is found that the velocity of this type of reaction varies considerably from one solvent to another, the variation involving both the $A$ and the $E$ factor. If the solvent used is of low polarity, the addition of small concentrations of a polar substance often has a marked effect on both $P$ and $E$.[18] This polar substance may in some cases be one of the reactants or the products, in which case the reaction will not follow simple kinetics.[19] The accelerating effect of polarisable material appears particularly clearly when attempts are made to study reactions of this type in the gas phase. It is invariably found that any homogeneous reaction which may be taking place is completely obscured by a much faster wall reaction, the energy necessary to produce the polar transition state being presumably lowered by the proximity of the material of which the reaction vessel is made.[20]

A semi-quantitative treatment resembling that already given shows that reactions between ions of like charge also involve a transition state which is solvated to a greater extent than the initial reactants, thus explaining the experimental values of $A \sim 10^{11}$. The general problem of reactions between ions can also be approached from an electrostatic standpoint, the solvent being regarded as a uniform medium of dielectric constant $D$. This leads to the equation

$$\log P = (z_1 z_2 e^2/krD^2) \,.\, \mathrm{d}D/\mathrm{d}T$$

where $e$ is the electronic charge, $r$ the distance of closest approach of the reacting ions, and $z_1$ and $z_2$ the algebraic valencies of the ions. ($P$ is the " experimental " value obtained by applying the simple Arrhenius equation to the experimental data. In principle it will vary slightly with temperature, but the variations will normally be too small to detect by experiment.) For polar solvents $\mathrm{d}D/\mathrm{d}T$ is negative, and this treatment therefore predicts $P < 1$ for reactions between ions of like charge and $P > 1$ for reactions between ions of opposite charge. This is of course in agreement with experiment, and the experimental values of $P$ can be accounted for by assuming plausible values for the distance $r$.[21] At first sight this method of treatment appears to bear no relation to the one given above, which appeals to changes in the orientation of solvent molecules. However, this orientation presupposes that the solvent molecules have a dipole moment, and it is the dipole moment which determines the magnitude of the factor $\mathrm{d}D/\mathrm{d}T$ in the above equation : hence the two methods have essentially the same physical basis, in spite of their apparent diversity.

The electrostatic treatment can also be formally applied to reactions involving uncharged molecules, giving an equation which involves the dipole moments and radii of the reactants and of the transition state.[22] However, the dipole moment of the transition state is not known, and the radii enter the equation to the third power, so the treatment does not yield anything of quantitative value. Qualitatively it agrees with experiment and with the orientation picture in predicting $P < 1$ for reactions with a transition state of high polarity.

It is of interest now to consider the reasons why reactions in solutions have proved in many respects more tractable than reactions in gases, both from an experimental and from a theoretical point of view, in spite of the additional complications introduced by the presence of the solvent. The almost complete absence of surface reactions is easily explained, since the solvent molecules, present in very large numbers, are likely to have the monopoly of adsorption on any surfaces which are present. Similarly, a chain reaction is unlikely to occur, since the usual chain carriers, atoms or free radicals, are likely to react with a solvent molecule before they are able to continue the chain by meeting another solute molecule. Much more important, however, is the rôle of the solvent molecules in maintaining the equilibrium distribution of energy among the reacting molecules. This distribution is bound to be disturbed to some extent by the reaction process, which removes molecules having an abnormally high energy, or an unusual distribution of energy among different internal degrees of freedom. Whether or not this disturbance is appreciable depends upon the rate at which the equilibrium distribution is re-established by the transfer of energy by collision, or among internal degrees of freedom. In gas reactions collisions are relatively rare, and the reaction velocity may be considerably affected by the rate at which energy is transferred, thus leading to apparent reaction orders between 1 and 2. In solution, on the other hand, the molecules of the reactant are colliding very frequently with solvent molecules, and it is probably safe to assume that there are no appreciable deviations from the equilibrium distribution. This assumption is in fact made, explicitly or implicitly, in all the theoretical considerations so far advanced. This is obvious in the case of the transition state method, which applies primarily only to a system in complete equilibrium, *e.g.*, $\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{X} \rightleftharpoons \mathrm{C} + \mathrm{D}$. Its application to observed velocities in systems not at equilibrium assumes that the velocity constants do not depend on the distance from equilibrium. It is perhaps not always realised that the equations of the simple collision theory are equally dependent on an equilibrium distribution, since expressions like $e^{-E/RT}$ are derived on the assumption of statistical equilibrium. The success of the general survey given above thus provides a further reason for supposing that equilibrium considerations are adequate for treating reaction velocities in solution. It should, however, be mentioned that many of the points already dealt with can be given an alternative explanation by assuming that the transfer of energy is a rate-determining factor.[23] The question cannot be regarded as definitely settled, but the non-equilibrium explanation seems unlikely in view of the frequent collisions with solvent molecules, and the many points of analogy between kinetic and thermodynamic data for reactions in solution.[24]

We have just seen that any deviations from equilibrium energy distribution are likely to be much less important in solution reactions than in gas reactions. The act of reaction will also tend to disturb the equilibrium spatial distribution of the reacting molecules, since it removes pairs of molecules which are close together, and it can easily be seen that this disturbance will be more serious in solution than in the gas phase. The production of fresh colliding pairs depends on the rate at which distant molecules can move towards each other, and this movement will be obstructed by the presence of solvent molecules. Under extreme conditions this process may not take place fast enough to maintain the equilibrium number of colliding pairs, and the reaction rate will then be partly controlled by the rate of diffusion through the solvent.[25] Such a state of affairs will arise if the viscosity is high, or if a large proportion of the collisions lead to reaction, *i.e.*, if the activation energy is low. It should be noted that this conclusion does not conflict with the previous statement that the collision number in solution does not differ greatly from that in the gas. In the absence of any reaction the total number of collisions is not much affected, but the presence of the solvent molecules causes them to occur in groups, so that when two solute molecules meet they are likely to collide a large number of times before part-

ing company.[26] It is because of this grouping that the removal of molecules by reaction may cause the collision number to fall below its equilibrium value.

Fortunately, rough calculations show that the lowering of the equilibrium collision number will not be appreciable in ordinary bimolecular reactions in solution. If $E = 20$ kg.-cals., the viscosity would have to approach that of the vitreous state before deviations became important, and for media of ordinary viscosity $E$ would have to be less than 2 kg.-cals.[27] This last value corresponds to a bimolecular reaction much too fast to be observed. There are, however, some observable phenomena in which a large proportion of collisions are effective, notably the coagulation of colloids under certain conditions,[28] and the quenching of fluorescence by solute molecules.[29] In both these cases the velocity should depend on the number of collision groups, rather than on the total number of collisions, and it is in fact found experimentally that the viscosity of the medium is an important factor. It should be emphasised that this class of phenomenon cannot be treated by the transition state theory. It is necessary to consider a kinetic picture of the collision process, taking into account the way in which the solvent modifies the simple picture used for gas reactions.

This lecture has been concerned chiefly with the general way in which reaction velocities in solution can be accounted for theoretically. Quantitative predictions are in most cases out of our reach at present, but there are a few points of detail on which notable success has been achieved, chiefly by using the transition state theory and by making use of the close relation which it indicates between kinetic and thermodynamic properties. I shall do little more than mention some of them here. The most notable instance is the primary salt effect in reactions between ions, which in dilute solutions can be quantitatively predicted by applying the Debye–Hückel theory. The correct expressions were given first by Brönsted in 1921, but during the following ten years there was much dispute about their theoretical basis.[30] The transition state theory composes these differences of opinion, and brings the problem into close relation with the secondary salt effect, *i.e.*, the effect of ionic concentration on the dissociation of a weak electrolyte.[31] The same kind of treatment can be extended to the effect of the dielectric constant on the velocity of ionic reactions,[32] the effect of salt concentration and dielectric constant on reactions involving dipole molecules,[33] and the effect of pressure on reaction kinetics in solution.[34] In all these cases, however, the resulting expressions involve unknown properties of the transition state, *e.g.*, its size and charge distribution, so no quantitative prediction is possible. It is more useful in these cases to regard the study of these different effects as a means of measuring the properties of the transition states in different reactions, with the ultimate aim of defining them as closely as we can stable molecular species.

In conclusion, I should like to mention three problems which have attracted a good deal of attention, but which are still far from being solved. When a reaction is studied in a series of solvents it is frequently found that the factors $A$ and $E$ of the Arrhenius equation change in a parallel manner. The transition state theory connects this behaviour in a natural manner with the parallelism between heats and entropies of solution which is found experimentally in many cases. In neither case, however, can any satisfactory molecular explanation be given.[35] Similarly, relations are often found to exist between reaction velocities and equilibrium constants in related series of reactions, corresponding to relations between free energies of activation and free energies of reaction. Examples of this kind of relation are the Brönsted equation for catalysis by a series of acids or bases, and the Tafel relation for over-voltage. In these cases it is possible to obtain a plausible explanation in terms of molecular potential-energy curves, but the detailed working out of this picture is far from satisfactory.[36] Finally, a strict theoretical treatment indicates that the observed activation energy should vary slightly with temperature, just like the energy of reaction in a chemical equilibrium.[37] At present there are very few pieces of experimental work in which this variation can be estimated, or even detected with certainty. Further work along these lines should give valuable information about the modes of vibration and rotation of the transition state, and the possibility of the kind of non-classical behaviour known as the "tunnel effect."[38]

The Tilden lectures are supposed to deal with recent advances in some branch of chemistry, and I may seem to have transgressed this requirement by attempting to give a complete survey of the theory of reaction kinetics in solution. My excuse must be the very rapid growth of the subject, and in fact almost every piece of work which I have mentioned has been done during the last ten years. It may also have been noticed that I have mentioned very few names in the course of the lecture. This is because a large number of workers in different countries have made significant contributions to the subject, and it is impossible to pick out one or two as specially worthy of mention. The recent history of this subject provides a very good example of the efficiency of unplanned collaboration, and several of the advances have been due to contributions from apparently irrelevant sources. Another ten years of work will inevitably fill out and modify many of the details, but I believe that the general outlines of the subject are now sufficiently well established to justify an attempt to review the position at this stage.

[1] *Nature*, 1942.
[2] Brönsted, *Chem. Rev.*, 1928, **5**, 231.
[3] Soper and Williams, J., 1931, 2297.
[4] Cf. Hinshelwood and Winkler, J., 1936, 371.
[5] For references see Bell, *Ann. Reports*, 1939, **36**, 86.
[6] Cf. discussions in J., 1937, 629, and *Trans. Faraday Soc.*, 1938, **34**, 1–267.
[7] Bell, *ibid.*, p. 232.
[8] Jowett, *Phil. Mag.*, 1929, **8**, 1059; Rabinowitch, *Trans. Faraday Soc.*, 1937, **33**, 1224; Fowler and Slater, *ibid.*, 1938, **34**, 91; Bell, *ibid.*, 1939, **35**, 324.

[9] *Nature*, 1936, **137**, 496; 1937, **138**, 368; 1937, **139**, 669; J., 1936, 1028; 1939, 870; *Trans. Faraday Soc.*, 1938, **34**, 128.
[10] Farkas and Sachsse, *Z. physikal. Chem.*, 1933, *B*, **23**, 1; Farkas and Garbatski, *Trans. Faraday Soc.*, 1939, **35**, 263.
[11] Evans and Polanyi, *ibid.*, 1936, **32**, 1333.
[12] Evans and Polanyi, *ibid.*, 1935, **31**, 875; Wynne-Jones and Eyring, *J. Chem. Physics*, 1935, **3**, 492.
[13] Bell, *Trans. Faraday Soc.*, 1939, **35**, 324.
[14] Wynne-Jones and Eyring, *loc. cit.* (12).
[15] Ogg and Rice, *J. Chem. Physics*, 1937, **5**, 140.
[16] Cf. Watson, *Ann. Reports*, 1938, **35**, 208.
[17] Criegee, Kraft, and Rank, *Annalen*, 1933, **507**, 159; Waters, J., 1939, 1805; Bell, Sturrock, and Whitehead, J., 1940, 82.
[18] Williams and Hinshelwood, J., 1934, 1079; Fairclough and Hinshelwood, J., 1937, 1573.
[19] Moelwyn-Hughes and Hinshelwood, J., 1932, 231; Pickles and Hinshelwood, J., 1936, 1353; Edwards, *Trans. Faraday Soc.*, 1937, **33**, 295; Holzschmidt and Potapov, *Acta Physicochim. U.R.S.S.*, 1937, **7**, 778.
[20] Bell and Burnett, *Trans. Faraday Soc.*, 1939, **35**, 208.
[21] Moelwyn-Hughes, *Proc. Roy. Soc.*, 1936, *A*, **155**, 308; LaMer and Kamner, *J. Amer. Chem. Soc.*, 1935, **57**, 2662.
[22] Moelwyn-Hughes and Sherman, J., 1936, 101.
[23] Hinshelwood, *Trans. Faraday Soc.*, 1936, **32**, 970; Edwards, *ibid.*, 1937, **33**, 295.
[24] Evans and Polanyi, *ibid.*, 1936, **32**, 1333.
[25] Leontovitch, *Z. Physik*, 1928, **50**, 58.
[26] Rabinowitch and Wood, *Trans. Faraday Soc.*, 1936, **32**, 1381; Rabinowitch, *ibid.*, 1937, **33**, 1225; Fairclough and Hinshelwood, J., 1939, 593.
[27] Evans and Polanyi, *loc. cit.* (24).
[28] Smoluchowski, *Physikal. Z.*, 1917, **17**, 594; *Z. physikal. Chem.*, 1917, **92**, 129.
[29] Wawilow, *Z. Physik*, 1929, **53**, 665; Franck and Wawilow, *ibid.*, 1931, **69**, 100; Svesnikov, *Acta Physicochim. U.R.S.S.*, 1935, **3**, 257; 1936, **4**, 453; 1937, **7**, 755; Bowen, *Trans. Faraday Soc.*, 1939, **35**, 15.
[30] Cf. Bell, *Ann. Reports*, 1934, **31**, 67.
[31] Wynne-Jones and Eyring, *loc. cit.* (12).
[32] See Davis and LaMer, *J. Chem. Physics*, 1942, **10**, 585, for references to earlier papers.
[33] Moelwyn-Hughes, *loc. cit.* (21); Laidler and Eyring, *Ann. New York Acad. Sci.*, 1940, **39**, 303; Amis and Jaffe, *J. Chem. Physics*, 1942, **10**, 599.
[34] Perrin, *Trans. Faraday Soc.*, 1938, **34**, 144.
[35] Bell, *ibid.*, 1937, **33**, 496; Hinshelwood, *ibid.*, 1938, **34**, 138.
[36] Bell, "Acid–Base Catalysis," Chap. VIII (Oxford, 1941).
[37] Scheffer and Brandsma, *Rec. Trav. chim.*, 1926, **45**, 522; Brandsma, *ibid.*, 1928, **47**, 94; 1929, **48**, 1205; LaMer, *J. Chem. Physics*, 1933, **1**, 289.
[38] Bell, *Proc. Roy. Soc.*, 1935, *A*, **148**, 241; Hirschfelder and Wigner, *J. Chem. Physics*, 1939, **7**, 616.

---

## 168. *Preparation of* 2 : 3-*Dinitronaphthalene and of* 3-*Nitro*-2-*naphthylamine.*

By Herbert H. Hodgson and Harold S. Turner.

2 : 3-Dinitronaphthalene has been readily obtained by deamination of 2 : 3-*dinitro*-1-*naphthylamine*, and reduced to 3-*nitro*-2-*naphthylamine*. NN′-*Ditoluene*-p-*sulphonyl*-1 : 4-*naphthylenediamine* could not be nitrated, and 2 : 3-dinitro-1 : 4-naphthylenediamine could not be deaminated.

Mononitration of 3-nitroaceto-1-naphthalide by nitric acid (*d* 1·5) below −3° gave 2 : 3-dinitroaceto-1-naphthalide, which was hydrolysed in ethyl alcohol–sulphuric acid to 2 : 3-*dinitro*-1-*naphthylamine*, diazotisation and deamination then yielding 2 : 3-dinitronaphthalene. The m. p. 159° could not be raised to that, 170·5—171° (*Chem. Listy*, 1926, **20**, 509), given by Chudozilov. Monoreduction gave 3-*nitro*-2-*naphthylamine*, which, unlike 2-nitro-1- and 1-nitro-2-naphthylamine, is soluble in dilute hydrochloric acid, behaviour which constitutes evidence in favour of single-bond union between the 2- and the 3-carbon atom of the nucleus.

3-Nitro-2-naphthylamine, like all the nitro-2-naphthylamines, is red, although it exhibits chromoisomerism; contrary to expectation, 2 : 3-dinitro-1-naphthylamine also is red, although both 2-nitro- and 3-nitro-1-naphthylamine are yellow.

### Experimental.

2 : 3-*Dinitro*-1-*naphthylamine*.—3-Nitro-1-naphthylamine (10 g.), boiled in glacial acetic acid (90 c.c.) and acetic anhydride (10 c.c.) for 3 minutes, was converted into 3-nitroaceto-1-naphthalide (10·6 g.). This compound (10 g.) was stirred gradually into nitric acid (60 c.c., *d* 1·5) below −3° and the mixture kept at −6° for 90 minutes and then poured on ice (300 g.). The precipitated 2 : 3-dinitroaceto-1-naphthalide (9·0 g.), after one crystallisation from glacial acetic acid, had m. p. 275° (Hodgson and Elliott, J., 1936, 1153, give m. p. 275·5°). It (11 g.) was refluxed with 50% sulphuric acid (35 c.c.) and ethyl alcohol (45 c.c.) for 2 hours and the mixture stirred into ice-water (350 c.c.). 2 : 3-*Dinitro*-1-*naphthylamine* (9·4 g.), precipitated in almost theoretical yield, was washed, dried in a vacuum, and crystallised from methyl alcohol containing 5% of acetone, forming deep red needles, m. p. 160—161° (Found : N, 18·0. $C_{10}H_7O_4N_3$ requires N, 18·0%).

2 : 3-*Dinitronaphthalene*.—A solution of 2 : 3-dinitro-1-naphthylamine (5·0 g.) in glacial acetic acid (35 c.c.) was stirred below 20° into one of sodium nitrite (2·0 g.) in sulphuric acid (15 c.c., *d* 1·84); the diazo-solution was kept for 30 minutes and then run into a suspension of cuprous oxide (8·0 g.) in ethyl alcohol (60 c.c.), the temperature rising to 60°. When the reaction had subsided, a further quantity of cuprous oxide (6·0 g.) was added, the mixture stirred for 10 minutes, water (1 l.) added, and the excess of alcohol and ethyl acetate distilled in steam. 2 : 3-Dinitronaphthalene was obtained from the dried precipitate by extraction with hot ethylene dichloride (50 c.c.) and charcoal, concentration of the extract, dilution with ligroin, and distillation at 10—15 mm. of the brown crystalline solid (1·8 g.) which had separated. Two crystallisations from aqueous acetic acid, distillation at 200°/10—15 mm., and further crystallisations from glacial acetic acid and aqueous acetone gave creamy-white needles, m. p. 159° (Found : N, 12·9. Calc. : N, 12·85%).

1 : 2-Dinitronaphthalene, prepared for comparison, crystallised from glacial acetic acid in stout colourless needles, m. p. 161—162° (Veselý and Dvorák, *Bull. Soc. chim.*, 1923, **33**, 319, describe pale brown needles, m. p. 158°) (Found: N, 12·9. Calc.: N, 12·8%), depressed to 121—122° by 2 : 3-dinitronaphthalene.

3-*Nitro*-2-*naphthylamine*.—2 : 3-Dinitronaphthalene (1·0 g.), suspended in methyl alcohol (15 c.c.), was refluxed on the water-bath during the dropwise addition of a solution of hydrated sodium sulphide (1·75 g.) and sodium bicarbonate (0·5 g.) in the minimum quantity of water. After boiling for 20 minutes, the mixture was poured on ice (200 g.) and kept for 2 days at 0°; the precipitate was collected and extracted with 10% hydrochloric acid (in 20 c.c. portions) until the extract, on being made alkaline with dilute aqueous ammonia at 0°, ceased to develop colour. The combined extracts were cooled and basified at 0° with dilute aqueous ammonia; after 5 hours, the crude nitro-amine, which had separated in deep red micro-needles (0·32 g.), was collected and dried in a vacuum. 3-*Nitro*-2-*naphthylamine* crystallised from ligroin as a mixture of red and orange-yellow needles, which all became red below the m. p. 86·5° (Found: N, 15·0. $C_{10}H_8O_2N_2$ requires N, 14·9%).

The *picrate*, obtained from the nitro-amine and a slight excess of picric acid in boiling ethyl alcohol, formed grey-green nodules, m. p. 171—172° (decomp. at 205—210°) (Found: N, 17·1. $C_{10}H_8O_2N_2,C_6H_3O_7N_3$ requires N, 16·8%).

3-*Nitroaceto*-2-*naphthalide*, obtained by boiling the nitro-amine (0·1 g.) with glacial acetic acid (1 c.c.) and acetic anhydride (0·15 c.c.) for 2 minutes and pouring the mixture on ice (20 g.), crystallised from aqueous acetic acid (charcoal) in cream needles, m. p. 191·5—192·5° (Found: N, 12·5. $C_{12}H_{10}O_3N_2$ requires N, 12·2%).

NN′-*Ditoluene*-p-*sulphonyl*-1 : 4-*naphthylenediamine*.—Toluene-*p*-sulphon-1-naphthalide (50 g.) in ice-cold aqueous sodium hydroxide solution was coupled with diazotised aniline, and the resulting azo-compound reduced in aqueous-alcoholic medium by the gradual addition of sodium hyposulphite (hydros) in presence of sodium carbonate. After removal of aniline with steam, the light brown precipitate of *N*-monotoluene-*p*-sulphonyl-1 : 4-naphthylenediamine (yield, 44—49 g.; 84—93%) had m. p. 186° after crystallising from aqueous acetic acid (cf. Morgan, E.P. 160,853). NN′-*Ditoluene*-p-*sulphonyl*-1 : 4-*naphthylenediamine* was obtained when the monoacylated compound (85·5 g.) was ground with toluene-*p*-sulphonyl chloride (85 g.), and the mixture heated on the water-bath with water (500 c.c.), sodium carbonate being added as required to remove free acid. After 3 hours' heating, the solid was collected, washed, and extracted, while being heated on the water-bath, with a mixture of 20% aqueous sodium hydroxide (250 c.c.) and water (1500 c.c.). From the filtered extract, the diacylated diamine was precipitated by carbon dioxide as a heavy crystalline powder (93·5 g.; 74·6% yield), which crystallised from glacial acetic acid in pinkish prisms, m. p. 249—250° (Found: N, 6·05. $C_{24}H_{22}O_4N_2S_2$ requires N, 6·00%). It resisted nitration by all the customary methods.

*Improved Methods for the Preparation of* 2 : 3-*Dinitro*-1 : 4-*naphthylenediamine and Intermediate Compounds*.—*N*-Acetyl-1 : 4-naphthylenediamine (53 g.) was obtained by reduction of 4-benzeneazoaceto-1-naphthalide (80 g.) with sodium hyposulphite (200 g.) in a boiling mixture of ethyl alcohol (360 c.c.) and saturated aqueous sodium carbonate (96 c.c.), followed by passage of steam to remove alcohol and aniline. Acetylation by dissolution in hot glacial acetic acid containing acetic anhydride afforded *NN′*-diacetyl-1 : 4-naphthylenediamine (cf. Hodgson and Elliott, J., 1936, 1764). This compound (10 g.) was stirred during 45 minutes into nitric acid (60 c.c., *d* 1·5) below −5°, and the mixture kept for 2 hours at −5° to −10° and then poured on ice (1000 g.), giving 2 : 3-dinitro-*NN′*-diacetyl-1 : 4-naphthylenediamine (cf. Hodgson and Elliott, J., 1936, 1152). Hydrolysis of the compound (5·0 g.) by 3 hours' refluxing with hydrochloric acid (30 c.c., *d* 1·16) and glacial acetic acid (30 c.c.) gave 2 : 3-dinitro-1 : 4-naphthylenediamine (cf. Hodgson and Elliott, *loc. cit.*), which resisted deamination by the customary methods.

The authors thank I.C.I. (Dyestuffs) Ltd. for gifts of chemicals.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, June 2nd*, 1943.]

---

## 169. *Physical Properties and Chemical Constitution. Part VIII. Alkyl Chlorides, Bromides, and Iodides.*

By ARTHUR I. VOGEL.

Determinations have been made of the refractive indices for the C, D, F, and G′ lines at 20·0°, and of the surface tensions and densities over a range of temperatures, of a wide series of alkyl chlorides, bromides, and iodides. The molecular refractivities and parachors have been evaluated, and the results for the *n*-halides used for the calculation of the $CH_2$ differences. These differ appreciably from the values hitherto accepted.

IN spite of its importance for the calculation of physical constants, no systematic investigation of the physical properties of alkyl chlorides, bromides, and iodides is on record. The data used by Eisenlohr (*Z. physikal. Chem.*, 1911, **75**, 605) for evaluation of the refractivities are limited and not always satisfactory. With regard to the parachors, Sugden ("The Parachor and Valency," 1930, p. 37) gives a table incorporating the data from which the constant for chlorine has been computed; the eight values range from 52·0 to 57·7, and the compounds include chloroform and carbon tetrachloride, which, in the author's opinion, should not be used in the initial deduction of the constant. (This subject will be discussed in a later paper.) Furthermore, for bromine and iodine, no experimental figures are disclosed and publication is confined to the statement (*op. cit.*, p. 189) "From organic compounds F = 25·7, Cl = 54·3, Br = 68·0, I = 91·0" (compare Sugden, J., 1924, **125**, 1180): these are based on a $CH_2$ value of 39·0.

The author has determined the refractivities and parachors of a large number of alkyl halides. The chlorides were prepared by means of both zinc chloride–hydrochloric acid (cf. Norris and Taylor, *J. Amer. Chem. Soc.*, 1924, **46**, 753) and thionyl chloride (cf. Clark and Streight, *Trans. Roy. Soc. Canada*, 1929, **23**, 77). The results for chlorides are in Table I, the straight-chain and branched-chain members being separated.

The purest samples of ethyl, propyl, and butyl bromides were obtained by use of concentrated hydrobromic acid (Norris, *J. Amer. Chem. Soc.*, 1916, **38**, 1075; *Amer. Chem. J.*, 1907, **38**, 639). Bromides from *n*-amyl to *n*-nonyl were prepared by means of hydrobromic acid–sulphuric acid (cf. Kamm and Marvel, *J. Amer. Chem. Soc.*, 1920, **42**, 299; "Organic Syntheses," 1921, **1**, 5), but purification was best effected up to *n*-octyl bromide

TABLE I.

| | *P.* | $R_C$. | $R_D$. | $R_F$. | $R_G$. | $Mn_D^{20°}$. |
|---|---|---|---|---|---|---|
| *Pr$^\alpha$Cl | 191·7 | 20·76 | 20·85 | 21·09 | 21·25 | 109·03 |
| *Bu$^\alpha$Cl | 230·3 | 25·30 | 25·42 | 25·70 | 25·92 | 129·75 |
| *Am$^\alpha$Cl | 270·2 | 29·92 | 30·06 | 30·38 | 30·61 | 150·51 |
| †$C_6H_{13}{}^\alpha$Cl | 310·5 | 34·58 | 34·74 | 35·13 | 35·41 | 171·27 |
| †$C_7H_{15}{}^\alpha$Cl | 350·7 | 39·16 | 39·33 | 39·77 | 40·07 | 191·97 |
| †$C_8H_{17}{}^\alpha$Cl | 390·2 | 43·76 | 43·96 | 44·44 | 44·78 | 212·70 |
| †$C_9H_{19}{}^\alpha$Cl | 431·0 | 48·46 | 48·68 | 49·22 | 49·61 | 233·31 |
| †$C_{10}H_{21}{}^\alpha$Cl | 472·0 | 53·11 | 53·36 | 53·94 | 54·25 | 254·03 |
| †$C_{11}H_{23}$Cl | 511·9 | 57·68 | 57·96 | 58·58 | 59·04 | 274·68 |
| †$C_{12}H_{25}$Cl | 549·7 | 62·27 | 62·55 | 63·22 | 63·74 | 295·42 |
| *Pr$^\beta$Cl | 191·9 | 20·89 | 20·99 | 21·23 | 21·41 | 108·25 |
| †Bu$^\beta$Cl | 228·2 | 25·26 | 25·38 | 25·67 | 25·88 | 129·73 |
| †*sec.*-BuCl | 229·5 | 25·39 | 25·51 | 25·80 | 26·00 | 129·33 |
| *tert.*-BuCl | 229·4 | 25·57 | 25·69 | 25·99 | 26·20 | 128·37 |
| *‡Am$^\beta$Cl | 268·8 | 30·05 | 30·19 | 30·52 | 30·76 | 150·21 |
| §Am$^\beta$Cl | 269·2 | 30·10 | 30·24 | 30·58 | 30·82 | 150·14 |
| *CHMePr$^\alpha$Cl | 268·4 | 29·97 | 30·11 | 30·45 | 30·69 | 150·08 |
| *CHEt$_2$Cl | 269·4 | 30·02 | 30·16 | 30·50 | 30·73 | 150·12 |
| *CMe$_2$EtCl | 268·2 | 30·07 | 30·22 | 30·55 | 30·80 | 149·79 |

* $ZnCl_2$–HCl method. † $SOCl_2$ method.
‡ From fermentation *iso*amyl alcohol (Bisol). § From synthetic *iso*amyl alcohol (Sharples).

by washing with concentrated hydrochloric acid (McCullough and Cortese, *J. Amer. Chem. Soc.*, 1929, **51**, 225) instead of concentrated sulphuric acid. The hydrochloric acid purification is not satisfactory for *n*-nonyl and higher bromides, which are best treated by methyl alcohol–sulphuric acid (Ruhoff, Burnett, and Reid, *ibid.*, 1934, **56**, 2784; "Organic Syntheses," 1935, **15**, 24). Bromides from *n*-octyl to *n*-dodecyl are best prepared with gaseous hydrogen bromide at 100—120° (cf. Ruzicka, Stoll, and Schinz, *Helv. Chim. Acta*, 1928, **11**, 685; Ruhoff, Burnett, and Reid, *locc. cit.*); Kamm and Marvel's method leads to carbonisation and gives lower yields (cf. "Organic Syntheses," 1921, **1**, 7). The most trustworthy results for bromides are in Table II, arranged as in Table I.

TABLE II.

| | *P.* | $R_C$. | $R_D$. | $R_F$. | $R_G$. | $Mn_D^{20}$. |
|---|---|---|---|---|---|---|
| *EtBr | 165·4 | 18·93 | 19·03 | 19·30 | 19·49 | 155·27 |
| *Pr$^\alpha$Br | 203·9 | 23·56 | 23·69 | 24·00 | 24·23 | 176·51 |
| *Bu$^\alpha$Br | 243·8 | 28·19 | 28·33 | 28·70 | 28·97 | 197·31 |
| †Am$^\alpha$Br | 283·1 | 32·81 | 32·99 | 33·39 | 33·70 | 218·30 |
| †$C_6H_{13}{}^\alpha$Br | 323·3 | 37·42 | 37·60 | 38·07 | 38·42 | 239·00 |
| †$C_7H_{15}{}^\alpha$Br | 363·5 | 42·05 | 42·26 | 42·77 | 43·15 | 259·80 |
| †$C_8H_{17}{}^\alpha$Br | 403·8 | 46·67 | 46·90 | 47·46 | 47·87 | 280·57 |
| ‡$C_9H_{19}{}^\alpha$Br | 444·1 | 51·24 | 51·49 | 52·09 | 52·55 | 301·28 |
| §$C_{10}H_{21}{}^\alpha$Br | 484·6 | 56·06 | 56·34 | 57·00 | 57·50 | 321·90 |
| §$C_{11}H_{23}{}^\alpha$Br | 523·7 | 60·47 | 60·77 | 61·48 | 62·01 | 342·70 |
| §$C_{12}H_{25}{}^\alpha$Br | 566·3 | 65·21 | 65·52 | 66·28 | 66·84 | 363·42 |
| *Pr$^\beta$Br | 205·1 | 23·83 | 23·96 | 24·29 | 24·53 | 175·34 |
| *Bu$^\beta$Br | 244·1 | 28·37 | 28·52 | 28·89 | 29·15 | 196·61 |
| **sec.*-BuBr | 243·5 | 28·42 | 28·57 | 28·94 | 29·23 | 196·86 |
| *‖Am$^\beta$Br | 280·6 | 32·80 | 32·97 | 33·39 | 33·70 | 217·86 |
| *¶Am$^\beta$Br | 282·6 | 32·95 | 33·12 | 33·53 | 33·91 | 217·83 |
| *CHMePr$^\alpha$Br | 280·9 | 32·80 | 32·97 | 33·39 | 33·70 | 217·81 |
| *CHEt$_2$Br | 281·7 | 32·90 | 33·07 | 33·49 | 33·80 | 218·01 |

* HBr method and HCl purification. † HBr–$H_2SO_4$ method and HCl purification.
‡ HBr–$H_2SO_4$ method and MeOH–$H_2SO_4$ purification. § HBr gas method and MeOH–$H_2SO_4$ purification.
‖ From fermentation *iso*amyl alcohol (Bisol). ¶ From synthetic *iso*amyl alcohol (Sharples).

TABLE III.

| | *P.* | $R_C$. | $R_D$. | $R_F$. | $R_G$. | $Mn_D^{20°}$. |
|---|---|---|---|---|---|---|
| MeI | 146·9 | 19·10 | 19·25 | 19·65 | 19·96 | 217·40 |
| EtI | 186·6 | 24·07 | 24·20 | 24·66 | 25·03 | 236·11 |
| Pr$^\alpha$I | 226·2 | 28·73 | 28·94 | 29·45 | 29·86 | 255·92 |
| Bu$^\alpha$I | 264·6 | 33·27 | 33·49 | 34·05 | 34·50 | 276·01 |
| Am$^\alpha$I | 305·1 | 37·99 | 38·23 | 38·84 | 39·32 | 296·18 |
| $C_6H_{13}{}^\alpha$I | 345·8 | 42·61 | 42·87 | 43·53 | 44·04 | 316·55 |
| $C_7H_{15}{}^\alpha$I | 386·6 | 47·29 | 47·57 | 48·28 | 48·84 | 336·84 |
| $C_8H_{17}{}^\alpha$I | 425·7 | 51·81 | 52·11 | 52·88 | 53·47 | 357·55 |
| Pr$^\beta$I | 225·9 | 29·11 | 29·33 | 29·88 | 30·27 | 254·88 |
| Bu$^\beta$I | 264·7 | 33·33 | 33·66 | 34·12 | 34·57 | 275·29 |
| *sec.*-BuI | 266·6 | 33·71 | 33·95 | 34·54 | 35·02 | 275·88 |
| *Am$^\beta$I | 302·7 | 38·05 | 38·29 | 38·90 | 39·38 | 295·64 |
| †Am$^\beta$I | 304·3 | 37·96 | 38·20 | 38·81 | 39·30 | 295·88 |
| CHMePr$^\alpha$I | 301·8 | 38·08 | 38·33 | 38·97 | 39·47 | 296·32 |
| CHEt$_2$I | 302·1 | 38·18 | 38·44 | 39·08 | 39·60 | 296·65 |

* From fermentation *iso*amyl alcohol (Bisol). † From synthetic *iso*amyl alcohol (Sharples).

The purest iodides (methyl to *n*-octyl) were prepared by distillation of the purified alcohols with constant-b. p. hydriodic acid (Norris, *loc. cit.*, 1907), followed by washing with concentrated hydrochloric acid: traces of iodine were removed by distillation from pure silver powder. If a *large* excess of yellow phosphorus is used in the ordinary phosphorus–iodine method (cf. Walker, J., 1892, **61**, 717; Adams and Voorhees, *J. Amer. Chem. Soc.*, 1919, **41**, 789; "Organic Syntheses," 1933, **13**, 60), small quantities of phosphorus compounds may be formed, which cannot be removed by simple distillation. The results for iodides, arranged as in Table I, are in Table III.

The new data for *n*-alkyl halides have been used for the evaluation of the $CH_2$ differences by the method of least squares: in the iodide series, methyl iodide has been omitted from the calculation, as it appears anomalous. The results are below. These values differ appreciably from the hitherto accepted figures (*P* 39·0, Sugden, J., 1924, 125, 1180; $R_C$ 4·598, $R_D$ 4·618, $R_F$ 4·668, $R_G$ 4·710, Eisenlohr, *Z. physikal. Chem.*, 1911, **75**, 605) which form the basis of the calculation of atomic and structural constants for the parachor and refractivities. The subject will be discussed further in a subsequent communication.

| | *P*. | $R_C$. | $R_D$. | $R_F$. | $R_G$. | $Mn_D^{20°}$. |
|---|---|---|---|---|---|---|
| Chlorides | 40·10 | 4·621 | 4·641 | 4·691 | 4·734 | 20·71 |
| Bromides | 40·02 | 4·625 | 4·646 | 4·696 | 4·733 | 20·79 |
| Iodides | 39·98 | 4·631 | 4·656 | 4·707 | 4·743 | 20·24 |

## Experimental.

*Physical Measurements.*—Full details are given in Part VII (this vol., p. 18). Unless otherwise stated, all b. p.'s are corrected.

*Previous Work.*—Parachor values, the source of which is not indicated, are taken from Sidgwick, Sugden, and Adam (*Brit. Assoc. Rep.*, 1932, 265). Reference is also made to what appear to be the most trustworthy recorded values of the refractive indices for comparison; the measurements of Timmermans and his co-workers and of Deffet have been reduced to 20° with the aid of their temperature coefficients.

*Alcohols.*—All the liquid alcohols, except methyl and ethyl, were dried with A.R. potassium carbonate and fractionated through a special Pyrex Young fractionating column with bark corks. Burrough's alcohols: A.R. absolute methyl and ethyl alcohols. British Industrial Solvents ("Bisol") alcohols: *n*-propyl, b. p. 96—97°/760 mm.; *iso*propyl, b. p. 82—82·5°/760 mm.; *n*-butyl, b. p. 116—117°/750 mm.; *iso*butyl, b. p. 106·5—107·5°/766 mm.; *iso*amyl, b. p. 131°/763 mm. (fermentation). Boake Roberts's alcohols: *sec.*-butyl, b. p. 100—100·5°/770 mm.; *tert.*-butyl, b. p. 81·5—82·5°/761 mm., m. p. 25·5°. Sharples's alcohols: *n*-amyl, b. p. 136·5—137·5°/766, mainly 137°/766 mm.; *iso*amyl, b. p. 130—130·5°/762 mm. (synthetic); methyl-*n*-propylcarbinol, b. p. 118·5°/764 mm.; diethylcarbinol, b. p. 115·5—116°/760 mm.; *tert.*-amyl (dimethylethylcarbinol), b. p. 101—101·5°/760 mm. Carbide and Carbon Chemicals (General and Metallurgical): *n*-hexyl alcohol, b. p. 156—157°/752 mm. *n*-Heptyl alcohol, b. p. 175·5—176·5°/774 mm., was prepared by reduction of redistilled *n*-heptaldehyde with iron and acetic acid ("Organic Syntheses," 1926, **6**, 52). Deutsche Hydrierwerke alcohols: *n*-octyl, b. p. 193—194°/763·5 mm.; *n*-nonyl, b. p. 211·5—212°/765 mm.; *n*-decyl, b. p. 228—229°/760 mm.; *n*-undecyl, b. p. 241—245°/769 mm.; *n*-dodecyl, m. p. 24°.

*Preparation of Alkyl Chlorides.*—(1) Norris and Taylor's method (*loc. cit.*) was modified as follows. The mixture of alcohol (1 g.-mol.), zinc chloride sticks (2 g.-mols.), and concentrated hydrochloric acid (2 g.-mols.) was heated for 4 hours over a free flame in a flask fitted with a long double-surface reflux condenser; the mixture was allowed to cool, and a double-surface condenser was attached to the top of the reflux condenser by a glass tube bent twice at right angles and arranged vertically so that the lower end was inside a flask cooled externally by ice. The alkyl chloride was then directly distilled from the reaction mixture: for *n*- and *iso*-propyl chlorides the water in the reflux condenser was maintained at 50—60°, but for the higher chlorides the water was removed. For purification, washing with concentrated hydrochloric acid in the cold is satisfactory for *n*-propyl and all *sec.*-alkyl chlorides, but refluxing and distillation with an equal volume of concentrated sulphuric acid was used for *n*-butyl and *n*-amyl chlorides. All the crude chlorides were washed with water, dilute sodium hydroxide or sodium carbonate solution, water, then dried with anhydrous sodium sulphate or calcium chloride (shaking) and fractionated, a middle fraction being collected. The yields of crude chlorides were: $Pr^{\alpha}Cl$ 92; $Pr^{\beta}Cl$ 72; $Bu^{\alpha}Cl$ 65 (by modification of method of "Organic Syntheses," 1925, **5**, 27); $Bu^{\beta}Cl$ 5*; *sec.*-BuCl 78; $Am^{\alpha}Cl$ 67; $Am^{\beta}Cl$ 52; $CHMePr^{\alpha}Cl$ 49; $CHEt_2Cl$ 55%.

(2) (*a*) To a mixture of the alcohol (0·5 g.-mol.) and pure pyridine (0·5 g.-mol.) in a 500-c.c. round-bottomed flask carrying a dropping funnel and double-surface reflux condenser, was added redistilled thionyl chloride (1 g.-mol.) during 3—4 hours (occasional shaking). The mixture was refluxed for ½ hr. and allowed to cool, and the upper layer separated,† treated with water, 5% sodium hydroxide solution, water, dried with anhydrous sodium sulphate, and fractionated. The yields of chlorides were: $Bu^{\alpha}Cl$ 33 g.; $Bu^{\beta}Cl$ 31 g.; *sec.*-BuCl 22 g.

(2) (*b*) When pyridine was omitted, the apparatus consisted of a 250-c.c. Pyrex Claisen flask carrying a dropping funnel and double-surface condenser (calcium chloride guard tubes); the side arm was plugged with a small cork, and the whole apparatus inclined so that the side tube was at an angle of 120°. For *n*-hexyl chloride, the redistilled thionyl chloride (1·5 g.-mols.) was placed in the flask, and the alcohol (0·5 g.-mol.) added with frequent shaking during 2—3 hours. In all other cases the alcohol (0·33 or 0·5 g.-mol.) was in the flask and the thionyl chloride (1 or 1·5 g.-mols.) was added dropwise. For *n*-undecyl and *n*-dodecyl chlorides, 4 g.-mols. of thionyl chloride were used to 1 g.-mol. of alcohol. The mixture was refluxed for 4—8 hours, the condenser, dropping funnel, and plug in the side-arm were then removed, and the mixture distilled. The crude chloride was washed with water, 10% sodium carbonate solution, water (twice), dried with anhydrous sodium sulphate, and fractionated. The yields of crude chlorides were: $C_6H_{13}{}^{\alpha}Cl$ 63; $C_7H_{15}{}^{\alpha}Cl$ 80; $C_8H_{17}{}^{\alpha}Cl$ 80; $C_9H_{19}{}^{\alpha}Cl$ 76; $C_{10}H_{21}{}^{\alpha}Cl$ 91; $C_{11}H_{23}{}^{\alpha}Cl$ 89; $C_{12}H_{25}{}^{\alpha}Cl$ 84%.

The tertiary chlorides were prepared from *tert.*-butyl and *tert.*-amyl alcohol by treatment with concentrated hydrochloric acid (see "Organic Syntheses," 1928, **8**, 50), dried by prolonged mechanical shaking with anhydrous sodium sulphate, and fractionated. The yield of chloride was approximately equal to that of the alcohol employed.

* Clark and Streight, *loc. cit.*, claim a 15% yield of pure chloride. Although a poor yield of a fraction with approximately the correct b. p. could be isolated, the main product was a high-boiling liquid.

† With *sec.*-butyl chloride, the liquid was so dark that the line of demarcation could not be seen. Accordingly, a volume (83 c.c.) equal to that for *n*-butyl chloride was run off, and the residual liquid treated as above.

**50.*** n-*Propyl chloride* (Method 1). B. p. 46—46·5°/764 mm.; *M* 78·55; $n_C$ † 1·38610, $n_D$ 1·38800, $n_F$ 1·39300, $n_G$ 1·39636. Densities determined: $d_{4°}^{20°}$ 0·8890, $d_{4°}^{40·7°}$ 0·8609. Apparatus *D*.

| *t.* | *h.* | *H.* | $d_{4°}^{t°}$. | *γ.* | *P.* | *t.* | *h.* | *H.* | $d_{4°}^{t°}$. | *γ.* | *P.* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 12·4° | 10·51 | 10·27 | 0·8982 | 22·78 | 191·3 | 41·6° | 9·29 | 9·05 | 0·8597 | 19·21 | 192·0 |
| 20·0 | 10·27 | 10·03 | 0·8890 | 22·02 | 191·7 | | | | | Mean | 191·7 |

(*P* 190·2, 187·0; Karvonen, *Ann. Acad. Sci. Fennicae*, 1912, [A], **3**, 1; 1914, [A], **5**, 128; *Chem. Zentr.*, 1912, II, 1271; 1919, III, 57, 807, gives b. p. 46·6°/770·5 mm., $d_{4°}^{20°}$ 0·8910, $n_C$ 1·38637, $n_D$ 1·38838, $n_F$ 1·39321, $n_G$ 1·39723; Timmermans and Hennaut-Roland, *J. Chim. physique*, 1930, **27**, 401, give b. p. 46·6°/760 mm., $d_{4°}^{20°}$ 0·89231, $n_C$ 1·38664, $n_F$ 1·39365, $n_G$ 1·39769.)

**51.** iso*Propyl chloride* (Method 1). B. p. 34·5°/740 mm.; *M* 78·55; $n_C$ 1·37612, $n_D$ 1·37810, $n_F$ 1·38298, $n_G$ 1·38651. Densities determined: $d_{4°}^{20°}$ 0·8629, $d_{4°}^{16·6°}$ 0·8657.

| *t.* | *h.* | *H.* | $d_{4°}^{t°}$. | *γ.* | *P.* | App. | *t.* | *h.* | *H.* | $d_{4°}^{t°}$. | *γ.* | *P.* | App. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 19·6° | 12·42 | 12·18 | 0·8633 | 19·69 | 192·1 | *A* | 24·4° | 9·69 | 9·45 | 0·8590 | 19·27 | 192·0 | *C* |
| 22·9 | 12·26 | 12·02 | 0·8603 | 19·36 | 191·9 | *A* | 25·6 | 9·59 | 9·35 | 0·8580 | 19·04 | 191·7 | *C* |
| 16·1 | 9·92 | 9·68 | 0·8663 | 19·91 | 191·9 | *C* | | | | | Mean | 191·9 | |

(Timmermans and Martin, *ibid.*, 1928, **25**, 413, give b. p. 34·8°/760 mm., $d_{4°}^{20°}$ 0·86167, $n_C$ 1·37625, $n_D$ 1·37835, $n_F$ 1·38340.)

**52.** n-*Butyl chloride* (Method 1). B. p. 77°/769 mm.; *M* 92·57; $n_C$ 1·39941, $n_D$ 1·40159, $n_F$ 1·40656, $n_G$ 1·41021. Densities determined: $d_{4°}^{20°}$ 0·8859, $d_{4°}^{41·7°}$ 0·8608, $d_{4°}^{60·8°}$ 0·8392. Apparatus *A*.

| *t.* | *h.* | *H.* | $d_{4°}^{t°}$. | *γ.* | *P.* | *t.* | *h.* | *H.* | $d_{4°}^{t°}$. | *γ.* | *P.* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 23·3° | 14·34 | 14·10 | 0·8821 | 23·29 | 230·5 | 61·0° | 12·18 | 11·94 | 0·8386 | 18·75 | 230·2 |
| 42·0 | 13·20 | 12·96 | 0·8605 | 20·88 | 230·2 | | | | | Mean | 230·3 |

(*P* 230·5; Karvonen, *loc. cit.*, gives b. p. 77·7—77·9°/763 mm., $d_{4°}^{20°}$ 0·88387, $n_C$ 1·39940, $n_D$ 1·40147, $n_F$ 1·40652, $n_G$ 1·41063; Timmermans and Hennaut-Roland, *loc. cit.*, give b. p. 78·50°/760 mm., $d_{4°}^{20°}$ 0·88647, $n_C$ 1·40026, $n_F$ 1·40713, $n_G$ 1·41161.)

**52A.** n-*Butyl chloride* (Method 2*a*). B. p. 78·0°/762 mm.; $n_C$ 1·40014, $n_D$ 1·40223, $n_F$ 1·40730, $n_G$ 1·41099; $R_C$ 25·32, $R_D$ 25·43, $R_F$ 25·72, $R_G$ 25·87; $Mn_D^{20°}$ 129·80. Densities determined: $d_{4°}^{20°}$ 0·8866, $d_{4°}^{40·9°}$ 0·8650, $d_{4°}^{60·6°}$ 0·8427. Apparatus *D*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 19·0 | 11·02 | 10·88 | 0·8877 | 23·85 | 229·9 | 41·0 | 10·19 | 9·95 | 0·8649 | 21·25 | 230·1 |
| 26·3 | 10·87 | 10·63 | 0·8799 | 23·10 | 230·1 | 61·6 | 9·45 | 9·21 | 0·8416 | 19·14 | 230·3 |
| | | | | | | | | | | Mean | 230·1 |

**53.** iso*Butyl chloride* (Method 2*a*). B. p. 68·5°/756 mm.; *M* 92·57; $n_C$ 1·39634, $n_D$ 1·39841, $n_F$ 1·40348, $n_G$ 1·40729. Densities determined: $d_{4°}^{20°}$ 0·8810, $d_{4°}^{40·5°}$ 0·8587, $d_{4°}^{58·4°}$ 0·8379. Apparatus *D*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 25·5 | 10·27 | 10·23 | 0·8750 | 21·66 | 228·3 | 56·5 | 9·03 | 8·79 | 0·8400 | 18·23 | 228·4 |
| 41·1 | 9·58 | 9·34 | 0·8580 | 19·79 | 227·9 | | | | | Mean | 228·2 |

(Timmermans and Martin, *J. Chim. physique*, 1926, **23**, 746, give b. p. 68·85°/760 mm., $d_{4°}^{20°}$ 0·87735, $n_C$ 1·39624, $n_D$ 1·39836, $n_F$ 1·40349, $n_G$ 1·40779.)

**54.** sec.-*Butyl chloride* (Method 2*a*). B. p. 68°/761 mm.; *M* 92·57; $n_C$ 1·39503, $n_D$ 1·39709, $n_F$ 1·40215, $n_G$ 1·40582. Densities determined: $d_{4°}^{20°}$ 0·8740, $d_{4°}^{40·7°}$ 0·8512. Apparatus *A*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 19·7 | 13·58 | 13·34 | 0·8743 | 21·84 | 228·9 | 40·5 | 12·61 | 12·37 | 0·8514 | 19·72 | 229·8 |
| 26·0 | 13·36 | 13·12 | 0·8676 | 21·32 | 229·7 | | | | | Mean | 229·5 |

(Timmermans and Martin, *loc. cit.*, 1928, give b. p. 68·25°/760 mm., $d_{4°}^{20°}$ 0·87320, $n_C$ 1·3949, $n_D$ 1·3970, $n_F$ 1·4020, $n_G$ 1·4064.)

**54A.** sec.-*Butyl chloride* (Method 1). B. p. 68°/769 mm.; $n_C$ 1·39486, $n_D$ 1·39694, $n_F$ 1·40197, $n_G$ 1·40558; $R_C$ 25·40, $R_D$ 25·54, $R_F$ 25·83, $R_G$ 26·04; $Mn_D^{20°}$ 129·31. Densities determined: $d_{4°}^{20°}$ 0·8726, $d_{4°}^{41·7°}$ 0·8478, $d_{4°}^{60·8°}$ 0·8250. Apparatus *A*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 12·4 | 14·20 | 13·96 | 0·8813 | 23·04 | 230·1 | 41·4 | 12·74 | 12·50 | 0·8481 | 19·85 | 230·8 |
| 20·7 | 13·72 | 13·48 | 0·8718 | 22·01 | 230·1 | 60·5 | 11·63 | 11·39 | 0·8253 | 17·60 | 230·5 |
| | | | | | | | | | | Mean | 230·4 |

**55.** tert.-*Butyl chloride* (HCl method). B. p. 49·5°/738 mm.; *M* 92·57; $n_C$ 1·38362, $n_D$ 1·38564, $n_F$ 1·39071, $n_G$ 1·39427. Densities determined: $d_{4°}^{20°}$ 0·8457, $d_{4°}^{43·6°}$ 0·8164. Apparatus *B*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 9·1 | 10·40 | 10·16 | 0·8596 | 20·48 | 229·3 | 40·6 | 8·94 | 8·70 | 0·8195 | 16·72 | 229·1 |
| 17·1 | 10·10 | 9·86 | 0·8493 | 19·64 | 229·7 | | | | | Mean | 229·4 |

(Timmermans and Martin, *J. Chim. physique*, 1934, **31**, 85, give b. p. 50·7°/760 mm., $d_{4°}^{20°}$ 0·84139, $n_C$ 1·38297, $n_F$ 1·39024; *P* 231·2.)

* The numbering of compounds in Clarendon type follows on from Part VII (this vol., p. 18).

† All the measurements of the refractive indices were carried out at 20° ± 0·02°. Where 20° is used, 20·0° is to be understood; $n_C$, $n_D$, $n_F$, $n_G$ are to be taken as referring to $n_0^{20·0°}$, etc.; $R_C$, etc., to $[R_L]_C$, etc. These abbreviations also apply to the data from the literature.

**56.** n-*Amyl chloride* (Method 1). B. p. 105°/764 mm.; *M* 106·60; $n_C$ 1·40961, $n_D$ 1·41177, $n_F$ 1·41691, $n_G$ 1·42053. Densities determined: $d_4^{20°}$ 0·8821, $d_4^{40·7°}$ 0·8600, $d_4^{62·9°}$ 0·8374, $d_4^{86·5°}$ 0·8125. Apparatus *D*.

| *t.* | *h.* | *H.* | $d_4^t$. | *γ.* | *P.* | *t.* | *h.* | *H.* | $d_4^t$. | *γ.* | *P.* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 12·9 | 11·95 | 11·75 | 0·8895 | 25·81 | 270·1 | 62·7 | 10·09 | 9·85 | 0·8376 | 20·38 | 270·4 |
| 23·0 | 11·56 | 11·32 | 0·8789 | 24·57 | 270·0 | 87·1 | 9·09 | 8·85 | 0·8119 | 17·75 | 270·1 |
| 41·9 | 10·82 | 10·58 | 0·8588 | 22·44 | 270·1 | | | | | Mean | 270·2 |

(*P* 270·4; Karvonen, *loc. cit.*, gives b. p. 105·7—105·8°/759 mm., $d_4^{20°}$ 0·87815, $n_C$ 1·40978, $n_D$ 1·41192, $n_F$ 1·41704, $n_G$ 1·42133; Lek, Thesis, Brussels, 1930, gives $d_4^{20°}$ 0·88159.)

**57.** iso*Amyl chloride* (Method 1, from Bisol fermentation *iso*amyl alcohol). B. p. 99°/777 mm.; *M* 106·60; $n_C$ 1·40696, $n_D$ 1·40909, $n_F$ 1·41425, $n_G$ 1·41799. Densities determined: $d_4^{20°}$ 0·8732, $d_4^{41·6°}$ 0·8521, $d_4^{61·4°}$ 0·8315, $d_4^{86·8°}$ 0·8050. Apparatus *A*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 14·6 | 14·96 | 14·72 | 0·8786 | 24·22 | 269·2 | 62·6 | 12·58 | 12·34 | 0·8308 | 19·18 | 268·9 |
| 18·3 | 14·63 | 14·39 | 0·8749 | 23·57 | 268·5 | 87·3 | 11·33 | 11·09 | 0·8043 | 16·70 | 268·0 |
| 41·6 | 13·67 | 13·43 | 0·8521 | 21·43 | 269·2 | | | | | Mean | 268·8 |

(P 269·8.)

**57A.** iso*Amyl chloride* (Method 1, from Sharples's synthetic *iso*amyl alcohol). B. p. 98·5°/765 mm.; $n_C$ 1·40627, $n_D$ 1·40840, $n_F$ 1·41361, $n_G$ 1·41738; $R_C$ 30·10, $R_D$ 30·24, $R_F$ 30·58, $R_G$ 30·82; $Mn_D^{20°}$ 150·14. Densities determined: $d_4^{20°}$ 0·8704, $d_4^{40·2°}$ 0·8492, $d_4^{59·6°}$ 0·8292. Apparatus *A*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 18·4 | 14·64 | 14·40 | 0·8721 | 23·52 | 269·2 | 40·3 | 13·54 | 13·30 | 0·8491 | 21·15 | 269·2 |
| 22·9 | 14·45 | 14·21 | 0·8674 | 23·08 | 269·4 | 60·9 | 12·48 | 12·24 | 0·8278 | 18·97 | 269·0 |
| | | | | | | | | | | Mean | 269·2 |

**58.** *β-Chloropentane* (Method 1). B. p. 97°/770 mm.; *M* 106·60; $n_C$ 1·40579, $n_D$ 1·40791, $n_F$ 1·41308, $n_G$ 1·41678. Densities determined: $d_4^{20°}$ 0·8732, $d_4^{40·8°}$ 0·8514, $d_4^{61·8°}$ 0·8308. Apparatus *A*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 17·8 | 14·62 | 14·38 | 0·8755 | 23·57 | 268·3 | 42·0 | 13·41 | 13·17 | 0·8502 | 20·97 | 268·5 |
| 19·5 | 14·53 | 14·29 | 0·8737 | 23·38 | 268·3 | 61·7 | 12·45 | 12·21 | 0·8309 | 19·00 | 268·2 |
| 24·8 | 14·36 | 14·12 | 0·8683 | 22·96 | 268·7 | | | | | Mean | 268·4 |

**59.** *γ-Chloropentane* (Method 1). B. p. 96°/753 mm.; *M* 106·60; $n_C$ 1·40609, $n_D$ 1·40820, $n_F$ 1·41336, $n_G$ 1·41709. Densities determined: $d_4^{20°}$ 0·8723, $d_4^{42·4°}$ 0·8509, $d_4^{59·6°}$ 0·8327. Apparatus *A*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 19·8 | 14·80 | 14·56 | 0·8725 | 23·79 | 269·8 | 41·5 | 13·64 | 13·40 | 0·8518 | 21·37 | 269·3 |
| 22·1 | 14·67 | 14·43 | 0·8712 | 23·54 | 269·5 | 63·0 | 12·51 | 12·27 | 0·8293 | 19·05 | 269·0 |
| 27·0 | 14·48 | 14·24 | 0·8673 | 23·13 | 269·5 | | | | | Mean | 269·4 |

**60.** tert.-*Amyl chloride* (HCl method). B. p. 84·5°/759 mm.; *M* 106·60; $n_C$ 1·40304, $n_D$ 1·40520, $n_F$ 1·41032, $n_G$ 1·41403. Densities determined: $d_4^{20°}$ 0·8650, $d_4^{40·5°}$ 0·8444, $d_4^{61·6°}$ 0·8215. Apparatus *D*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 17·8 | 10·86 | 10·62 | 0·8673 | 22·75 | 268·4 | 41·1 | 9·99 | 8·75 | 0·8438 | 20·32 | 268·5 |
| 23·3 | 10·62 | 10·38 | 0·8616 | 22·09 | 268·2 | 61·2 | 9·11 | 8·87 | 0·8219 | 18·00 | 267·7 |
| | | | | | | | | | | Mean | 268·2 |

**61.** n-*Hexyl chloride* (Method 2*b*). B. p. 134°/759 mm.; *M* 120·62; $n_C$ 1·41774, $n_D$ 1·41991, $n_F$ 1·42525, $n_G$ 1·42907. Densities determined: $d_4^{20°}$ 0·8784, $d_4^{40·6°}$ 0·8600, $d_4^{61·3°}$ 0·8407, $d_4^{86·7°}$ 0·8163. Apparatus *A*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 20·3 | 16·18 | 15·94 | 0·8781 | 26·21 | 310·8 | 62·7 | 14·09 | 13·85 | 0·8394 | 21·77 | 310·4 |
| 20·4 | 16·14 | 15·90 | 0·8780 | 26·14 | 310·6 | 87·3 | 12·84 | 12·60 | 0·8157 | 19·25 | 309·7 |
| 42·6 | 15·19 | 14·95 | 0·8582 | 24·02 | 311·2 | | | | | Mean | 310·5 |

(Karvonen, *loc. cit.*, gives $d_4^{20°}$ 0·8755, $n_C$ 1·41731, $n_D$ 1·41944, $n_F$ 1·42464, $n_G$ 1·42893; Clark and Streight, *loc. cit.*, give b. p. 135—136°, $d_4^{20°}$ 0·8759, $n_D$ 1·42364; Lek, *loc. cit.*, gives b. p. 135·10°/760 mm., $d_4^{20°}$ 0·86595, $n_C$ 1·41648, $n_F$ 1·42408.)

**62.** n-*Heptyl chloride* (Method 2*b*). B. p. 159·5°/769 mm.; *M* 134·65; $n_C$ 1·42354, $n_D$ 1·42571, $n_F$ 1·43107, $n_G$ 1·43490. Densities determined: $d_4^{20°}$ 0·8766, $d_4^{41·3°}$ 0·8573, $d_4^{61·5°}$ 0·8398, $d_4^{87·0°}$ 0·8165. Apparatus *D*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 12·3 | 12·95 | 12·71 | 0·8835 | 27·73 | 349·7 | 62·3 | 11·30 | 11·06 | 0·8391 | 22·92 | 351·2 |
| 21·5 | 12·71 | 12·47 | 0·8752 | 26·95 | 350·5 | 87·2 | 10·46 | 10·22 | 0·8163 | 20·60 | 351·4 |
| 41·6 | 12·00 | 11·76 | 0·8570 | 24·89 | 350·9 | | | | | Mean | 350·7 |

(Clark and Streight, *loc. cit.*, give b. p. 158·5—159·5°, $d_4^{20°}$ 0·8741, $n_D$ 1·42844.)

**63.** n-*Octyl chloride* (Method 2*b*). B. p. 181·5°/765 mm.; *M* 148·68; $n_C$ 1·42836, $n_D$ 1·43058, $n_F$ 1·43596, $n_G$ 1·43990. Densities determined: $d_4^{20°}$ 0·8748, $d_4^{41·2°}$ 0·8565, $d_4^{61·2°}$ 0·8406, $d_4^{86·6°}$ 0·8192. Apparatus *D*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 17·9 | 13·17 | 12·93 | 0·8766 | 27·99 | 390·1 | 61·4 | 11·62 | 11·38 | 0·8406 | 23·62 | 390·0 |
| 22·5 | 13·02 | 12·78 | 0·8727 | 27·54 | 390·2 | 87·1 | 10·82 | 10·58 | 0·8188 | 21·39 | 390·5 |
| 41·3 | 12·32 | 12·08 | 0·8564 | 25·55 | 390·3 | | | | | Mean | 390·2 |

(Clark and Streight, *loc. cit.*, give b. p. 179—180°, $d_4^{20°}$ 0·8745, $n_D$ 1·43424.)

**64.** n-*Nonyl chloride* (Method 2*b*). B. p. 202°/760 mm.; *M* 162·70; $n_C$ 1·43175, $n_D$ 1·43400, $n_F$ 1·43946, $n_G$ 1·44348. Densities determined: $d_4^{20°}$ 0·8704, $d_4^{40·5°}$ 0·8551, $d_4^{61·1°}$ 0·8388, $d_4^{84·8°}$ 0·8204. Apparatus *D*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 17·3 | 13·52 | 13·28 | 0·8725 | 28·62 | 431·3 | 61·3 | 12·00 | 11·76 | 0·8386 | 24·36 | 431·0 |
| 20·4 | 13·35 | 13·11 | 0·8701 | 28·17 | 430·8 | 86·6 | 11·10 | 10·86 | 0·8190 | 21·97 | 430·1 |
| 41·4 | 12·78 | 12·54 | 0·8545 | 26·46 | 431·9 | | | | | Mean | 431·0 |

(Clark and Streight, *loc. cit.*, give b. p. 98—100°/23 mm., $d_4^{20°}$ 0·8679, $n_D$ 1·43692.)

**65.** n-*Decyl chloride* (Method 2*b*). B. p. 222—223°/760 mm.; *M* 176·73; $n_C$ 1·43502, $n_D$ 1·43731, $n_F$ 1·44281, $n_{G'}$ 1·44682. Densities determined: $d_4^{20°}$ 0·8683, $d_4^{41·6°}$ 0·8524, $d_4^{61·6°}$ 0·8372, $d_4^{85·4°}$ 0·8180. Apparatus *D*.

| *t.* | *h.* | *H.* | $d_{4°}^{t°}$. | *γ.* | *P.* | *t.* | *h.* | *H.* | $d_{4°}^{t°}$. | *γ.* | *P.* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 21·8 | 13·64 | 13·40 | 0·8679 | 28·72 | 471·4 | 63·0 | 12·27 | 12·03 | 0·8360 | 24·84 | 472·0 |
| 42·1 | 12·99 | 12·75 | 0·8516 | 26·81 | 472·3 | 86·3 | 11·49 | 11·25 | 0·8172 | 22·70 | 472·1 |
| | | | | | | | | | | Mean | 472·0 |

**66.** n-*Undecyl chloride* (Method 2*b*). B. p. 240—241°/772 mm.; *M* 190·75; $n_C$ 1·43778, $n_D$ 1·44003, $n_F$ 1·44559, $n_{G'}$ 1·44966. Densities determined: $d_4^{20°}$ 0·8677, $d_4^{41·4°}$ 0·8526, $d_4^{60·5°}$ 0·8378, $d_4^{85·1°}$ 0·8197. Apparatus *D*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 21·3 | 13·85 | 13·61 | 0·8677 | 29·13 | 511·3 | 61·5 | 12·60 | 12·36 | 0·8370 | 25·55 | 512·4 |
| 25·7 | 13·76 | 13·52 | 0·8635 | 28·83 | 511·9 | 87·3 | 11·76 | 11·52 | 0·8181 | 23·27 | 512·1 |
| 42·3 | 13·23 | 12·99 | 0·8517 | 27·32 | 512·0 | | | | | Mean | 511·9 |

**67.** n-*Dodecyl chloride* (Method 2*b*). B. p. 116·5°/5·0 mm.; *M* 204·78; $n_C$ 1·44028, $n_D$ 1·44255, $n_F$ 1·44814, $n_{G'}$ 1·45226. Densities determined: $d_4^{20°}$ 0·8673, $d_4^{41·2°}$ 0·8516, $d_4^{60·5°}$ 0·8377, $d_4^{86·4°}$ 0·8181. Apparatus *A*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 24·3 | 18·06 | 17·82 | 0·8641 | 28·83 | 549·2 | 61·9 | 16·45 | 16·21 | 0·8367 | 25·40 | 549·4 |
| 41·5 | 17·30 | 17·04 | 0·8514 | 27·17 | 549·1 | 86·9 | 15·53 | 15·29 | 0·8177 | 23·41 | 550·9 |
| | | | | | | | | | | Mean | 549·7 |

*Preparation of Alkyl Bromides.*—The methods used were: (1) The hydrogen bromide–sulphuric acid method (Kamm and Marvel, *locc. cit.*), A.R. hydrobromic acid (47·5%) being used with all the *n*-alcohols up to *n*-decyl and with *iso*propyl, *sec.*-butyl, and *iso*amyl alcohols, and methyl-*n*-propyl- and diethyl-carbinols. (2) Use of 47·5% A.R. hydrobromic acid (Norris, *locc. cit.*) with ethyl, *n*-propyl, *iso*propyl, *iso*butyl, *n*-butyl, *sec.*-butyl, and *iso*amyl alcohols: the method gave poor yields from *n*-amyl and higher *n*-alcohols. (3) The phosphorus tribromide method (Adams and Noller, *J. Amer. Chem. Soc.*, 1926, **48**, 1080; Reynolds and Adkins, *ibid.*, 1929, **51**, 280; "Organic Syntheses," 1933, **13**, 20) with *iso*propyl, *iso*butyl, *n*-amyl, and *n*-hexyl alcohols. (4) Ruhoff, Burnett, and Reid's gaseous hydrogen bromide method (*locc. cit.*) with *n*-octyl, *n*-decyl, *n*-undecyl, and *n*-dodecyl alcohols.

Preparations by method (1) were made on a large scale (to give 750—1000 g. of bromide). The refluxing period was 6—12 hours. For all bromides up to and including *n*-hexyl, the crude bromide could be distilled directly from the reaction mixture; for the higher bromides, where appreciable charring took place, the reaction product was filtered through glass-wool and diluted with water, and the crude bromide separated, best by ether extraction. All the bromides to *n*-octyl were purified by washing twice with an equal volume of concentrated hydrochloric acid (McCullough and Cortese, *loc. cit.*), then with water, 10% sodium carbonate solution, water (twice); they were then dried with calcium chloride and fractionated, a middle fraction being collected. For bromides beyond *n*-octyl, however, Ruhoff, Burnett, and Reid's method of purification (*loc. cit.*) must be used, as shown by the following observations for carefully fractionated samples:

$C_8H_{17}{}^aBr$ (Method 1), HCl purified: $d_4^{20°}$ 1·1124, $n_D^{20°}$ 1·4527.
$C_8H_{17}{}^aBr$ (Method 4), MeOH–$H_2SO_4$ purified: $d_4^{20°}$ 1·1104, $n_D^{20°}$ 1·4524.
$C_9H_{19}{}^aBr$ (Method 1), HCl purified: $d_4^{20°}$ 1·0823, $n_D^{20°}$ 1·4534.
$C_9H_{19}{}^aBr$ (Method 1), MeOH–$H_2SO_4$ purified: $d_4^{20°}$ 1·0901, $n_D^{20°}$ 1·4542.

In the preparation of *n*-propyl and *iso*propyl bromides by this method, the best yields are obtained by using the proportions described for *n*-butyl bromide but the slow-distillation technique given for ethyl bromide ("Organic Syntheses," 1921, **1**, 6); *e.g.*, distillation of 360 g. of *n*-propyl alcohol occupied 6 hours and the yield of bromide was 655 g., but if the mixture was refluxed first and then distilled, the yield was much lower.

Details of method (2) are illustrated by the preparation of ethyl bromide. A mixture of 31 g. of absolute alcohol and 460 g. of A.R. constant-b. p. hydrobromic acid in a 500-c.c. Pyrex distilling flask was slowly distilled (6 hrs.) from an air-bath, the distillate being collected in a receiver cooled in ice. The bromide layer (64 g.) was separated, the acid layer mixed with a further 31 g. of absolute alcohol, and again distilled (5 hrs.). The resultant bromide layer was separated, combined with that from the first distillation, and washed and dried as in method (1), a middle fraction being collected on distillation. The yields of crude products for the other bromides were: *n*-propyl 65; *iso*propyl 75, *n*-butyl 72, *iso*butyl 54, *sec.*-butyl 75; *iso*amyl (fermentation) 37%.

*iso*Propyl and *iso*butyl bromides were prepared in excellent yield at −10° to 0° by method (3), the crude product being purified by washing with concentrated hydrochloric or hydrobromic acid (instead of concentrated sulphuric acid), followed by water, 10% sodium carbonate solution, and water, and dried with anhydrous sodium sulphate. Contrary to Mann and Purdie (J., 1935, 1549), the product obtained from higher alcohols (*n*-amyl to *n*-octyl) at 0° was far from pure; it was necessary to complete the reaction (3 mols. of alcohol and 1·3 mols. of phosphorus tribromide) by refluxing for 2—3 hours: the cold product was poured into water, neutralised with 10% sodium hydroxide solution, and steam-distilled. The crude bromide was purified as described above. For higher *n*-alcohols this method is not as satisfactory as method (1) or (4).

Bromides of *n*-alcohols above heptyl were best prepared by method (4) at 100—120° (cf. "Organic Syntheses," 1935, **15**, 35), the crude bromide being purified by Ruhoff, Burnett, and Reid's method (*locc. cit.*): the formation of emulsions sometimes encountered in the subsequent treatment with 50% methyl alcohol was considerably reduced by addition of a few grams of anhydrous calcium chloride. The yields were excellent throughout.

**68.** *Ethyl bromide* (Method 2). B. p. 38·5°/765 mm.; *M* 108·98; $n_C$ 1·42212, $n_D$ 1·42481, $n_F$ 1·43146, $n_{G'}$ 1·43651. Density determined: $d_4^{20°}$ 1·4633. * = Apparatus *C*. † = Apparatus *D*.

| *t.* | *h.* | *H.* | $d_{4°}^{t°}$. | *γ.* | *P.* | *t.* | *h.* | *H.* | $d_{4°}^{t°}$. | *γ.* | *P.* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 18·8° | 6·96 | 6·72 | 1·4653 | 24·32 | 165·4 † | 18·2 | 7·26 | 7·02 | 1·4664 | 24·44 | 165·4 * |
| 25·2 | 6·81 | 6·57 | 1·4545 | 23·60 | 165·4 † | | | | | Mean | 165·4 |

[*P* 167·6 (e), 165·7; Timmermans and Martin, *J. Chim. physique*, 1926, **23**, 746, give b. p. 38·40°/760 mm., $d_4^{20°}$ 1·46063, $n_C$ 1·42195, $n_D$ 1·42476, $n_F$ 1·43135, $n_{G'}$ 1·43686.]

**68A.** *Ethyl bromide* (Method 1). B. p. 38°/756 mm.; $n_C$ 1·42197, $n_D$ 1·42466, $n_F$ 1·43135, $n_{G'}$ 1·43643; $R_C$ 18·96, $R_D$ 19·07, $R_F$ 19·33, $R_{G'}$ 19·54; $Mn_D^{20°}$ 155·26. Densities determined: $d_4^{20°}$ 1·4604, $d_4^{15·7°}$ 1·4676. * = Apparatus *C*. † = Apparatus *D*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 19·9 | 7·07 | 6·83 | 1·4606 | 23·68 | 164·8 * | 16·9 | 6·96 | 6·72 | 1·4656 | 24·32 | 165·3 † |
| 25·2 | 7·00 | 6·76 | 1·4517 | 23·30 | 165·2 * | 21·1 | 6·86 | 6·59 | 1·4586 | 23·74 | 165·1 |
| | | | | | | | | | | Mean | 165·1 |

**69.** n-*Propyl bromide* (Method 2). B. p. 72°/780 mm.; $M$ 123·01; $n_C$ 1·43218, $n_D$ 1·43485, $n_F$ 1·44143, $n_G$ 1·44640. Densities determined: $d_4^{20°}$ 1·3548, $d_4^{41·6°}$ 1·3185, $d_4^{61·6°}$ 1·3847. Apparatus *A*.

| *t.* | *h.* | *H.* | $d_{4°}^{t°}$. | *γ.* | *P.* | *t.* | *h.* | *H.* | $d_{4°}^{t°}$. | *γ.* | *P.* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 19·4 | 10·27 | 10·03 | 1·3558 | 25·46 | 203·8 | 25·3 | 10·11 | 9·87 | 1·3458 | 24·87 | 204·1 |
| 20·2 | 10·22 | 9·98 | 1·3545 | 25·31 | 203·7 | 42·5 | 9·42 | 9·18 | 1·3170 | 22·64 | 203·9 |
| | | | | | | | | | | Mean | 203·9 |

(*P* 205·3; Karvonen, *loc. cit.*, gives b. p. 70·8°/769·2 mm.; $d_4^{20°}$ 1·3539, $n_C$ 1·43142, $n_D$ 1·43411, $n_F$ 1·44055, $n_G$ 1·44591; Timmermans and Martin, *loc. cit.*, give b. p. 71·00°/760 mm., $d_4^{20°}$ 1·35135, $n_C$ 1·43180, $n_D$ 1·43435, $n_F$ 1·44119, $n_G$ 1·44684.)

**69A.** n-*Propyl bromide* (Method 1). B. p. 70·5°/752 mm.; $n_C$ 1·43208, $n_D$ 1·3425, $n_F$ 1·44136, $n_G$ 1·44637; $R_C$ 23·54, $R_D$ 23·72, $R_F$ 23·98, $R_G$ 24·21; $Mn_D^{20°}$ 176·43. Densities determined: $d_4^{20°}$ 1·3556, $d_4^{42·5°}$ 1·3153, $d_4^{61·9°}$ 1·2799. Apparatus *B*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 9·2 | 8·46 | 8·22 | 1·3750 | 26·50 | 203·0 | 41·2 | 7·52 | 7·28 | 1·3176 | 22·49 | 203·3 |
| 19·3 | 8·13 | 7·89 | 1·3569 | 25·05 | 203·3 | 61·5 | 7·00 | 6·76 | 1·2807 | 20·30 | 204·4 |
| | | | | | | | | | | Mean | 203·6 |

**70.** iso*Propyl bromide* (Method 2). B. p. 59°/758 mm.; $M$ 123·01; $n_C$ 1·42271, $n_D$ 1·42541, $n_F$ 1·43205, $n_G$ 1·43711. Densities determined: $d_4^{20°}$ 1·3138, $d_4^{40·6°}$ 1·2777. Apparatus *A*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 15·0 | 9·74 | 9·50 | 1·3246 | 23·56 | 204·8 | 41·4 | 8·82 | 8·58 | 1·2763 | 20·51 | 205·5 |
| 21·8 | 9·47 | 9·23 | 1·3106 | 22·60 | 205·0 | | | | | Mean | 205·1 |

(*P* 205·1; Timmermans and Martin, *loc. cit.*, 1928, give b. p. 59·35°/760 mm., $d_4^{20°}$ 1·31388, $n_C$ 1·42286, $n_D$ 1·42562, $n_F$ 1·43235, $n_G$ 1·43755.)

**70A.** iso*Propyl bromide* (Method 1). B. p. 58·9°/748 mm.; $n_C$ 1·42147, $n_D$ 1·42416, $n_F$ 1·43073, $n_G$ 1·43569; $R_C$ 23·97, $R_D$ 24·15, $R_F$ 24·42, $R_G$ 24·67; $Mn_D^{20°}$ 175·19. Densities determined: $d_4^{20°}$ 1·3030, $d_4^{40·7°}$ 1·2629. Apparatus *A*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 9·8 | 10·05 | 9·81 | 1·3227 | 24·30 | 206·5 | 40·7 | 8·82 | 8·58 | 1·2629 | 20·29 | 207·0 |
| 19·5 | 9·61 | 9·37 | 1·3040 | 22·88 | 206·5 | | | | | Mean | 206·7 |

**70B.** iso*Propyl bromide* (Method 3). B. p. 59·3°/756 mm.; $n_C$ 1·42321, $n_D$ 1·42591, $n_F$ 1·43238, $n_G$ 1·43730; $R_C$ 23·74, $R_D$ 23·87, $R_F$ 24·19, $R_G$ 24·42; $Mn_D^{20°}$ 175·40. Densities determined: $d_4^{20°}$ 1·3202, $d_4^{0·3°}$ 1·3325, $d_4^{42·1°}$ 1·2783. Apparatus *A*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 14·1 | 9·65 | 9·41 | 1·3314 | 23·46 | 203·4 | 41·2 | 8·71 | 8·47 | 1·2800 | 20·30 | 204·3 |
| 23·3 | 9·37 | 9·13 | 1·3140 | 22·46 | 204·8 | | | | | Mean | 203·9 |

**71.** n-*Butyl bromide* (Method 2). B. p. 101°/768 mm.; $M$ 137·03; $n_C$ 1·43732, $n_D$ 1·43993, $n_F$ 1·44637, $n_G$ 1·45125. Densities determined: $d_4^{20°}$ 1·2744, $d_4^{41·0°}$ 1·2474, $d_4^{60·6°}$ 1·2190. Apparatus *D*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 21·3 | 8·60 | 8·36 | 1·2738 | 26·28 | 243·7 | 41·1 | 8·08 | 7·84 | 1·2473 | 24·15 | 243·8 |
| 24·9 | 8·51 | 8·27 | 1·2685 | 25·91 | 243·7 | 60·6 | 7·53 | 7·29 | 1·2190 | 21·95 | 244·0 |
| | | | | | | | | | | Mean | 243·8 |

(*P* 243·5; Karvonen, *loc. cit.*, gives b. p. 100·2°/745·6 mm.; $d_4^{20°}$ 1·2746, $n_C$ 1·43719, $n_D$ 1·43983, $n_F$ 1·44613, $n_G$ 1·45150; Timmermans and Martin, *loc. cit.*, 1926, give b. p. 101·60°/760 mm., $d_4^{20°}$ 1·27567, $n_C$ 1·43690, $n_D$ 1·43975, $n_F$ 1·44615, $n_G$ 1·45145.)

**71A.** n-*Butyl bromide* (Method 1). B. p. 101°/758 mm.; $n_C$ 1·43733, $n_D$ 1·43993, $n_F$ 1·44637, $n_G$ 1·45125; $R_C$ 28·11, $R_D$ 28·26, $R_F$ 28·62, $R_G$ 28·89; $Mn_D^{20°}$ 197·31. Densities determined: $d_4^{20°}$ 1·2778, $d_4^{41·2°}$ 1·2476, $d_4^{60·5°}$ 1·2184, $d_4^{86·0°}$ 1·1804. Apparatus *A*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 26·1 | 11·07 | 10·83 | 1·2689 | 25·73 | 243·2 | 59·9 | 9·76 | 9·52 | 1·2193 | 21·74 | 243·0 |
| 40·3 | 10·49 | 10·25 | 1·2489 | 23·97 | 242·8 | 86·1 | 8·82 | 8·58 | 1·1803 | 18·96 | 243·0 |
| | | | | | | | | | | Mean | 243·0 |

**72.** iso*Butyl bromide* (Method 2). B. p. 91—91·5°/765 mm.; $M$ 137·03; $n_C$ 1·43214, $n_D$ 1·43475, $n_F$ 1·44115, $n_G$ 1·44594. Densities determined: $d_4^{20°}$ 1·2532, $d_4^{42·6°}$ 1·2205, $d_4^{63·0°}$ 1·1913, $d_4^{86·8°}$ 1·1548. Apparatus *D*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 12·5 | 8·48 | 8·24 | 1·2640 | 25·66 | 244·1 | 61·9 | 7·17 | 6·93 | 1·1929 | 20·42 | 244·6 |
| 41·5 | 7·64 | 7·40 | 1·2221 | 22·53 | 243·7 | | | | | Mean | 244·1 |

(*P* 243·8; Timmermans and Martin, *loc. cit.*, 1928, give b. p. 91·40°/760 mm., $d_4^{20°}$ 1·26462, $n_C$ 1·43394, $n_D$ 1·43664, $n_F$ 1·44317, $n_G$ 1·44871.)

**72A.** iso*Butyl bromide* (Method 3). B. p. 91—91·5°/745 mm.; $n_C$ 1·43228, $n_D$ 1·43490, $n_F$ 1·44129, $n_G$ 1·44612; $R_C$ 28·73, $R_D$ 28·88, $R_F$ 29·24, $R_G$ 29·52; $Mn_D^{20°}$ 196·62. Densities determined: $d_4^{20°}$ 1·2380, $d_4^{40·2°}$ 1·2077, $d_4^{60·4°}$ 1·1749. Apparatus *A*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 14·2 | 11·10 | 10·86 | 1·2469 | 25·36 | 246·6 | 40·5 | 10·20 | 9·96 | 1·2072 | 22·51 | 247·2 |
| 24·1 | 10·75 | 10·51 | 1·2317 | 24·24 | 246·9 | 60·4 | 9·35 | 9·11 | 1·1749 | 20·04 | 247·1 |
| | | | | | | | | | | Mean | 246·8 |

**73.** sec.-*Butyl bromide* (Method 2). B. p. 91°/764 mm.; $M$ 137·03; $n_C$ 1·43397, $n_D$ 1·43660, $n_F$ 1·44317, $n_G$ 1·44816. Densities determined: $d_4^{20°}$ 1·2556, $d_4^{41·8°}$ 1·2257, $d_4^{61·0°}$ 1·1977. Apparatus *A*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 19·3 | 10·82 | 10·58 | 1·2556 | 24·89 | 243·6 | 41·7 | 10·01 | 9·77 | 1·2258 | 22·43 | 243·3 |
| 37·3 | 10·21 | 9·97 | 1·2320 | 23·00 | 243·6 | 60·8 | 9·35 | 9·11 | 1·1980 | 20·44 | 243·6 |
| | | | | | | | | | | Mean | 243·5 |

(Timmermans and Delcourt, *loc. cit.*, give b. p. 91·2°/760 mm., $d_4^{20°}$ 1·26088, $n_C$ 1·43434, $n_F$ 1·44369, $n_G$ 1·44944; *P* 243·4.)

**73A.** sec.-*Butyl bromide* (Method 1). B. p. 91·5°/756 mm.; $n_C$ 1·43421, $n_D$ 1·43685, $n_F$ 1·44340, $n_G$ 1·44835; $R_C$ 28·34, $R_D$ 28·56, $R_F$ 28·86, $R_G$ 29·14; $Mn_D^{20°}$ 196·90. Densities determined: $d_4^{20°}$ 1·2597, $d_4^{41·5°}$ 1·2264, $d_4^{62·5°}$ 1·1935. Apparatus *B*.

| *t.* | *h.* | *H.* | $d_4^{t°}$. | *γ.* | *P.* | *t.* | *h.* | *H.* | $d_4^{t°}$. | *γ.* | *P.* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 10·9 | 9·02 | 8·78 | 1·2739 | 26·23 | 243·4 | 41·4 | 8·20 | 7·96 | 1·2266 | 22·89 | 244·4 |
| 22·2 | 8·75 | 8·51 | 1·2562 | 25·07 | 244·1 | 63·2 | 7·56 | 7·32 | 1·1925 | 20·47 | 244·8 |
| | | | | | | | | | | Mean | 244·2 |

**74.** n-*Amyl bromide* (Method 1). B. p. 128·5°/764 mm.; *M* 151·06; $n_C$ 1·44243, $n_D$ 1·44505, $n_F$ 1·45144, $n_G$ 1·45619. Densities determined: $d_4^{20°}$ 1·2190, $d_4^{41·1°}$ 1·1936, $d_4^{61·7°}$ 1·1673, $d_4^{89·5°}$ 1·1352. Apparatus *D*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 19·4 | 9·31 | 9·07 | 1·2197 | 27·32 | 283·2 | 60·8 | 8·23 | 7·99 | 1·1684 | 23·05 | 283·3 |
| 22·9 | 9·22 | 8·98 | 1·2154 | 26·95 | 283·2 | 87·5 | 7·48 | 7·24 | 1·1340 | 20·28 | 283·0 |
| 42·4 | 8·65 | 8·41 | 1·1920 | 24·76 | 282·7 | | | | | Mean | 283·1 |

(*P* 283·6; Karvonen, *loc. cit.*, gives b. p. 127·8—128·0°/762 mm., $d_4^{20°}$ 1·2175, $n_C$ 1·44175, $n_D$ 1·44435, $n_F$ 1·45067, $n_G$ 1·45592; Lek, *loc. cit.*, gives $d_4^{20°}$ 1·21730.)

**74A.** n-*Amyl bromide* (Method 3). B. p. 128·5°/762 mm.; $n_C$ 1·44200, $n_D$ 1·44460, $n_F$ 1·45103, $n_G$ 1·45579; $R_C$ 32·72, $R_D$ 32·89, $R_F$ 33·30, $R_G$ 33·60; $Mn_D^{20°}$ 218·22. Densities determined: $d_4^{20°}$ 1·2215, $d_4^{41·2°}$ 1·1954, $d_4^{60·4°}$ 1·1714, $d_4^{86·6°}$ 1·1368. Apparatus *D*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 20·2 | 9·33 | 9·09 | 1·2212 | 27·41 | 283·0 | 62·1 | 8·20 | 7·96 | 1·1693 | 22·99 | 282·9 |
| 42·0 | 8·74 | 8·50 | 1·1944 | 25·07 | 283·0 | 87·1 | 7·51 | 7·27 | 1·1362 | 20·40 | 282·7 |
| | | | | | | | | | | Mean | 282·9 |

**75.** iso*Amyl bromide* (Method 1, from Bisol alcohol). B. p. 119·5°/760 mm.; *M* 151·06; $n_C$ 1·43964, $n_D$ 1·44225, $n_F$ 1·44861, $n_G$ 1·45341. Densities determined: $d_4^{20°}$ 1·2127, $d_4^{40·9°}$ 1·1850, $d_4^{60·8°}$ 1·1594, $d_4^{87·3°}$ 1·1239. Apparatus *A*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 17·1 | 11·75 | 11·51 | 1·2165 | 26·22 | 281·0 | 63·2 | 10·08 | 9·84 | 1·1562 | 21·30 | 280·7 |
| 41·4 | 10·80 | 10·56 | 1·1843 | 23·42 | 280·6 | 87·6 | 9·15 | 8·91 | 1·1235 | 18·74 | 280·2 |
| | | | | | | | | | | Mean | 280·6 |

(*P* 282·9; Lek, *loc. cit.*, gives $d_4^{20°}$ 1·20300.)

**75A.** iso*Amyl bromide* (Method 1, from Sharples's synthetic alcohol). B. p. 119·5°/755 mm.; $n_C$ 1·43941, $n_D$ 1·44199, $n_F$ 1·44839, $n_G$ 1·45416; $R_C$ 32·95, $R_D$ 33·12, $R_F$ 33·53, $R_G$ 33·91; $Mn_D^{20°}$ 217·83. Densities determined: $d_4^{20°}$ 1·2069, $d_4^{41·8°}$ 1·1791, $d_4^{62·6°}$ 1·1529, $d_4^{87·4°}$ 1·1200. Apparatus *D*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 15·4 | 9·11 | 8·87 | 1·2128 | 26·57 | 282·8 | 60·5 | 7·90 | 7·66 | 1·1556 | 21·86 | 282·6 |
| 41·9 | 8·36 | 8·12 | 1·1790 | 23·64 | 282·5 | 86·4 | 7·20 | 6·96 | 1·1213 | 19·27 | 282·6 |
| | | | | | | | | | | Mean | 282·6 |

**76.** *β-Bromopentane* (Method 1). B. p. 117°/759 mm.; *M* 151·06; $n_C$ 1·43929, $n_D$ 1·44194, $n_F$ 1·44840, $n_G$ 1·45315. Densities determined: $d_4^{20°}$ 1·2122, $d_4^{41·5°}$ 1·1828, $d_4^{61·1°}$ 1·1577, $d_4^{84·8°}$ 1·1263. Apparatus *A*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 14·3 | 11·80 | 11·56 | 1·2198 | 26·40 | 280·7 | 62·1 | 10·11 | 9·87 | 1·1564 | 21·37 | 280·9 |
| 18·9 | 11·66 | 11·42 | 1·2137 | 25·92 | 280·8 | 86·5 | 9·26 | 9·02 | 1·1240 | 18·99 | 280·9 |
| 41·6 | 10·85 | 10·61 | 1·1827 | 23·50 | 281·2 | | | | | Mean | 280·9 |

**77.** *γ-Bromopentane* (Method 1). B. p. 118°/769 mm.; *M* 151·06; $n_C$ 1·44054, $n_D$ 1·44320, $n_F$ 1·44967, $n_G$ 1·45449. Densities determined: $d_4^{25°}$ 1·2051, whence $d_4^{20°}$ 1·2113 (extrap.), $d_4^{42·0°}$ 1·1831, $d_4^{64·0°}$ 1·1566, $d_4^{84·5°}$ 1·1293. Apparatus *D*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 23·3 | 8·83 | 8·59 | 1·2072 | 25·48 | 281·5 | 61·5 | 7·84 | 7·60 | 1·1597 | 21·94 | 281·9 |
| 27·3 | 8·73 | 8·49 | 1·2022 | 25·21 | 281·6 | 87·2 | 7·17 | 6·93 | 1·1257 | 19·27 | 281·4 |
| 41·0 | 8·43 | 8·19 | 1·1856 | 23·98 | 281·9 | | | | | Mean | 281·7 |

**78.** n-*Hexyl bromide* (Method 1). B. p. 153·5°/746 mm.; *M* 165·08; $n_C$ 1·44532, $n_D$ 1·44781, $n_F$ 1·45424, $n_G$ 1·45907. Densities determined: $d_4^{20°}$ 1·1748, $d_4^{40·6°}$ 1·1525, $d_4^{62·8°}$ 1·1269, $d_4^{86·3°}$ 1·0987. Apparatus *D*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 18·3 | 9·91 | 9·67 | 1·1767 | 28·10 | 323·0 | 61·1 | 8·82 | 8·58 | 1·1288 | 23·92 | 323·4 |
| 26·2 | 9·75 | 9·51 | 1·1677 | 27·42 | 323·5 | 85·9 | 8·11 | 7·87 | 1·0922 | 21·36 | 322·9 |
| 42·1 | 9·27 | 9·03 | 1·1508 | 25·66 | 323·6 | | | | | Mean | 323·3 |

(*P* 322·8; Karvonen, *loc. cit.*, gives $d_4^{20°}$ 1·1763, $n_C$ 1·44520, $n_D$ 1·44778, $n_F$ 1·45402, $n_G$ 1·45924; Lek, *loc. cit.*, gives b. p. 156·3°/760 mm., $d_4^{20°}$ 1·17988, $n_C$ 1·44478, $n_F$ 1·45380.)

**78A.** n-*Hexyl bromide* (Method 3). B. p. 153°/751 mm.; $n_C$ 1·44501, $n_D$ 1·44761, $n_F$ 1·45388, $n_G$ 1·45856; $R_C$ 37·49, $R_D$ 37·68, $R_F$ 38·14, $R_G$ 38·48; $Mn_D^{20°}$ 238·97. Densities determined: $d_4^{20°}$ 1·1718, $d_4^{41·5°}$ 1·1484, $d_4^{61·8°}$ 1·1250, $d_4^{89·1°}$ 1·0964. Apparatus *A*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 28·7 | 12·40 | 12·16 | 1·1621 | 26·46 | 322·2 | 61·2 | 11·46 | 11·22 | 1·1257 | 23·65 | 323·4 |
| 42·2 | 11·98 | 11·74 | 1·1476 | 25·23 | 322·4 | 86·5 | 10·55 | 10·31 | 1·0960 | 21·16 | 323·0 |
| | | | | | | | | | | Mean | 322·8 |

**79.** n-*Heptyl bromide* (Method 1). B. p. 177·5°/758 mm.; *M* 179·11; $n_C$ 1·44794, $n_D$ 1·45052, $n_F$ 1·45681, $n_G$ 1·46150. Densities determined: $d_4^{20°}$ 1·1401, $d_4^{41·9°}$ 1·1182, $d_4^{62·8°}$ 1·1046, $d_4^{86·7°}$ 1·0695. Apparatus *A*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 17·6 | 13·78 | 13·54 | 1·1426 | 28·97 | 363·7 | 61·8 | 12·42 | 12·18 | 1·1064 | 25·23 | 362·8 |
| 26·5 | 13·52 | 13·28 | 1·1333 | 28·25 | 364·1 | 85·7 | 11·39 | 11·15 | 1·0705 | 22·35 | 363·8 |
| 41·3 | 12·93 | 12·69 | 1·1188 | 26·58 | 363·5 | | | | | Mean | 363·5 |

(*P* 363·0; Deffet, *Bull. Soc. chim. Belg.*, 1931, **40**, 385, gives b. p. 180·0°/760 mm., $d_4^{20°}$ 1·13991, $n_C$ 1·44772, $n_F$ 1·45678, $n_G$ 1·46177.)

**80.** n-*Octyl bromide* (Method 1). B. p. 200°/768 mm.; *M* 193·14; $n_C$ 1·45010, $n_D$ 1·45267, $n_F$ 1·45893, $n_G$ 1·46356. Densities determined: $d_4^{20°}$ 1·1124, $d_4^{41·8°}$ 1·0918, $d_4^{61·1°}$ 1·0722, $d_4^{86·2°}$ 1·0454. Apparatus *D*.

| *t.* | *h.* | *H.* | $d_{4°}^{t°}$. | *γ.* | *P.* | *t.* | *h.* | *H.* | $d_{4°}^{t°}$. | *γ.* | *P.* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 19·2 | 10·88 | 10·64 | 1·1132 | 29·25 | 403·5 | 60·7 | 9·81 | 9·57 | 1·0726 | 25·35 | 404·0 |
| 22·3 | 10·79 | 10·55 | 1·1101 | 28·92 | 403·5 | 86·7 | 9·14 | 8·90 | 1·0449 | 22·97 | 404·6 |
| 42·0 | 10·29 | 10·05 | 1·0916 | 27·09 | 403·7 | | | | | Mean | 403·8 |

(*P* 402·4; Deffet, *loc. cit.*, gives b. p. 201·5°/760 mm., $d_4^{20°}$ 1·11290, $n_C$ 1·45011, $n_F$ 1·45921, $n_G$ 1·46435; Lek, *loc. cit.*, gives $d_4^{20°}$ 1·11293.)

**81.** n-*Nonyl bromide* (Method 1). B. p. 219·5°/745 mm.; *M* 207·18; $n_C$ 1·45165, $n_D$ 1·45417, $n_F$ 1·46044, $n_G$ 1·46513. Densities determined: $d_4^{20°}$ 1·0901, $d_4^{41·3°}$ 1·0699, $d_4^{61·5°}$ 1·0509, $d_4^{86·2°}$ 1·0270. Apparatus *A*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 17·7 | 14·82 | 14·58 | 1·0923 | 29·82 | 443·2 | 63·2 | 13·28 | 13·04 | 1·0493 | 25·62 | 444·2 |
| 41·8 | 14·00 | 13·76 | 1·0704 | 27·58 | 443·6 | 86·9 | 12·56 | 12·32 | 1·0263 | 23·68 | 445·3 |
| | | | | | | | | | | Mean | 444·1 |

(Tomecko and Adams, *J. Amer. Chem. Soc.*, 1927, **49**, 529, give b. p. 88°/4 mm., $d_4^{20°}$ 1·0183, $n_D$ 1·4533.)

**82.** n-*Decyl bromide* (Method 4). B. p. 102·5°/5·9 mm.; *M* 221·19; $n_C$ 1·45274, $n_D$ 1·45527, $n_F$ 1·46149, $n_G$ 1·46617. Densities determined: $d_4^{20°}$ 1·0658, $d_4^{42·6°}$ 1·0475, $d_4^{61·5°}$ 1·0286, $d_4^{87·6°}$ 1·0055. Apparatus *A*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 18·9 | 15·04 | 14·80 | 1·0668 | 29·56 | 483·5 | 40·9 | 14·38 | 14·14 | 1·0472 | 27·73 | 484·6 |
| 26·5 | 14·90 | 14·66 | 1·0600 | 29·09 | 484·6 | 61·8 | 13·73 | 13·49 | 1·0283 | 25·97 | 485·6 |
| | | | | | | | | | | Mean | 484·6 |

**83.** n-*Undecyl bromide* (Method 4). B. p. 114°/5·0 mm.; *M* 235·21; $n_C$ 1·45444, $n_D$ 1·45697, $n_F$ 1·46319, $n_G$ 1·46788. Densities determined: $d_4^{20°}$ 1·0541, $d_4^{41·0°}$ 1·0367, $d_4^{61·8°}$ 1·0196, $d_4^{86·7°}$ 0·9976. Apparatus *A*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 19·9 | 15·55 | 15·31 | 1·0542 | 30·22 | 523·1 | 41·0 | 14·83 | 14·59 | 1·0367 | 28·32 | 523·4 |
| 21·8 | 15·49 | 15·25 | 1·0526 | 30·06 | 523·3 | 62·5 | 14·19 | 13·95 | 1·0190 | 26·62 | 524·3 |
| 28·2 | 15·32 | 15·08 | 1·0472 | 29·57 | 523·8 | 85·7 | 13·36 | 13·12 | 0·9984 | 24·53 | 524·3 |
| | | | | | | | | | | Mean | 523·7 |

**84.** n-*Dodecyl bromide* (Method 4). B. p. 130·0°/5·7 mm.; *M* 249·24; $n_C$ 1·45556, $n_D$ 1·45807, $n_F$ 1·46426, $n_G$ 1·46878. Densities determined: $d_4^{20°}$ 1·0382, $d_4^{41·0°}$ 1·0208, $d_4^{59·7°}$ 1·0055, $d_4^{84·9°}$ 0·9839. Apparatus *D*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 19·3 | 12·31 | 12·07 | 1·0388 | 30·96 | 566·0 | 61·2 | 11·21 | 10·97 | 1·0043 | 27·21 | 566·8 |
| 24·9 | 12·11 | 11·87 | 1·0341 | 30·31 | 565·5 | 85·9 | 10·54 | 10·30 | 0·9831 | 25·01 | 566·9 |
| 40·6 | 11·74 | 11·50 | 1·0211 | 29·00 | 566·4 | | | | | Mean | 566·3 |

*Preparation of Alkyl Iodides.*—(1) This method consisted in slow distillation of the alcohol with 3—4 g.-mols. of constant-b. p. hydriodic acid ("Inorganic Syntheses," 1939, **1**, 157), the experimental details being similar to those already described for the bromides (see Norris, *loc. cit.*, 1907). For quantities of the order of 0·5 g.-mol. of alcohol the time required was 4—6 hours for $C_1$—$C_4$ iodides and 7—9 hours for $C_5$—$C_8$ iodides. The iodide was purified by washing with an equal volume of concentrated hydrochloric acid, then with water, 5% sodium carbonate or hydroxide solution until colourless, water (twice), and dried with anhydrous sodium sulphate or calcium chloride. For iodides up to $C_4$, the fractionated sample was usually shaken with pure silver powder, filtered, and redistilled immediately before use. Higher iodides were first distilled under normal pressure in dim light, the correct b. p. fraction removed (this was generally slightly coloured), shaken mechanically with silver powder, filtered, and distilled under diminished pressure. All the samples used were colourless and were kept in the dark until required. The results of the preparations are summarised below.

| Iodide, RI. | Wt. of ROH (g.). | Wt. of 57% HI (g.). | Yield of crude RI (g.). | Iodide, RI. | Wt. of ROH (g.). | Wt. of 57% HI (g.). | Yield of crude RI (g.). |
|---|---|---|---|---|---|---|---|
| MeI ..... | 16 | 302 | 61 | *Am$\beta$I ..... | 44 | 337 | 90 |
| EtI ..... | 44 | 302 | 80 | †Am$\beta$I ..... | 40 | 297 | 95 |
| Pr$^\alpha$I ..... | 30 | 302 | 84 | CHMePr$^\alpha$I ..... | 44 | 337 | 90 |
| Pr$^\beta$I ..... | 30 | 302 | 85 | CHEt$_2$I ..... | 40 | 297 | 81 |
| Bu$^\alpha$I ..... | 40 | 485 | 93 | $C_6H_{13}{}^\alpha$I ..... | 51 | 446 | 111 |
| Bu$^\beta$I ..... | 30 | 273 | 65 | $C_7H_{15}{}^\alpha$I ..... | 58 | 446 | 110 |
| *sec.*-BuI ..... | 30 | 273 | 73 | $C_8H_{17}{}^\alpha$I ..... | 65 | 446 | 120 |
| Am$^\alpha$I ..... | 44 | 337 | 99 | | | | |

* From Sharples's synthetic alcohol. † From Bisol fermentation alcohol.

(2) The iodides (to $C_8$) were generally also prepared by the red phosphorus–iodide method or by the large-scale method of Adams and Voorhees (*loc. cit.*; cf. Adams, Kamm, and Marvel, "Organic Chemical Reagents," Univ. of Illinois Bulletin, 1919, **1**, 27; "Organic Syntheses," 1933, **13**, 60) in which equal quantities of red and yellow phosphorus are used. A relative deficiency of iodine led to an impure product. In order to obtain the purest iodides by this method, only a slight excess of phosphorus should be used, and for iodides other than methyl and ethyl the best results are obtained with the proportions 3 g.-atoms of iodine, 1·22 g.-atoms of a mixture of red and yellow phosphorus (6 : 5), and 3·05 g.-mols. of alcohol.

**85.** *Methyl iodide* (Method 1). B. p. 42·3°/761 mm.; *M* 141·95; $n_C$ 1·52635, $n_D$ 1·53152, $n_F$ 1·54468, $n_G$ 1·55498. Densities determined: $d_4^{20°}$ 2·2829, $d_4^{16·5°}$ 2·2895. Apparatus *D*.

| *t.* | *h.* | *H.* | $d_{4°}^{t°}$. | *γ.* | *P.* | *t.* | *h.* | *H.* | $d_{4°}^{t°}$. | *γ.* | *P.* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 16·5 | 5·79 | 5·55 | 2·2895 | 31·38 | 146·8 | 22·9 | 5·68 | 5·44 | 2·2711 | 30·59 | 146·6 |
| | | | | | | | | | | Mean | 146·7 |

(*P* 146·2; Karvonen, *loc. cit.*, gives b. p. 42·2°/753 mm., $d_4^{17°}$ 2·2863, $n_C^{17°}$ 1·52787, $n_D^{17°}$ 1·53306, $n_F^{17°}$ 1·54607, $n_G^{17°}$ 1·55740; Timmermans and Delcourt, *loc. cit.*, 1934, give b. p. 42·5°/760 mm., $d_4^{20°}$ 2·27900, $n_C$ 1·52575, $n_F$ 1·54535.)

**85A.** *Methyl iodide* (Method 2). B. p. 42°/751 mm.; $n_C$ 1·52660, $n_D$ 1·53173, $n_F$ 1·54489, $n_G$ 1·55528; $R_C$ 19·12, $R_D$ 19·28, $R_F$ 19·67, $R_G$ 19·98; $Mn_D^{20°}$ 217·42. Densities determined: $d_4^{20°}$ 2·2819, $d_4^{14·1°}$ 2·2922. Apparatus $A$ = *. Apparatus $C$ = †.

| *t.* | *h.* | *H.* | $d_4^{t°}$. | *γ.* | *P.* | *t.* | *h.* | *H.* | $d_4^{t°}$. | *γ.* | *P.* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 14·1 | 7·44 | 7·20 | 2·2922 | 30·90 | 146·1 * | 16·0 | 5·94 | 5·70 | 2·2889 | 30·97 | 146·4 † |
| 21·4 | 7·21 | 6·97 | 2·2795 | 29·75 | 145·6 * | 22·2 | 5·73 | 5·49 | 2·2781 | 29·76 | 145·8 † |
| | | | | | | | | | | Mean | 146·0 |

**86.** *Ethyl iodide* (Method 1). B. p. 73°/765 mm.; $M$ 155·98; $n_C$ 1·50897, $n_D$ 1·51369, $n_F$ 1·52532, $n_G$ 1·53483. Densities determined: $d^{20°}$ 1·9395, $d_4^{41·8°}$ 1·8881, $d_4^{61·8°}$ 1·8419. Apparatus $A$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 13·3 | 8·33 | 8·09 | 1·9556 | 29·62 | 186·1 | 60·9 | 7·05 | 6·81 | 1·8441 | 23·52 | 186·7 |
| 41·1 | 7·65 | 7·41 | 1·8891 | 26·21 | 187·0 | | | | | Mean | 186·6 |

($P$ 187·0; Karvonen, *loc. cit.*, gives $d_4^{16·5°}$ 1·9427, $n_C^{16·5°}$ 1·51077, $n_D^{16·5°}$ 1·51542, $n_F^{16·5°}$ 1·52715, $n_G^{16·5°}$ 1·53726; Timmermans and Martin, *loc. cit.*, 1928, give b. p. 72·30°/760 mm., $d_4^{20°}$ 1·93582, $n_C$ 1·50899, $n_D$ 1·51367, $n_F$ 1·52541.)

**86A.** *Ethyl iodide* (Method 2). B. p. 71·5°/745 mm.; $n_C$ 1·50873, $n_D$ 1·51337, $n_F$ 1·52509, $n_G$ 1·53428; $R_C$ 24·04, $R_D$ 24·23, $R_F$ 24·69, $R_G$ 25·05; $Mn_D^{20°}$ 236·06. Densities determined: $d_4^{20°}$ 1·9361, $d_4^{40·9°}$ 1·8883, $d_4^{61·5°}$ 1·8394. Apparatus $D$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 14·4 | 6·43 | 6·19 | 1·9490 | 29·79 | 187·0 | 40·9 | 5·86 | 5·62 | 1·8883 | 26·21 | 187·1 |
| 22·8 | 6·30 | 6·06 | 1·9297 | 28·88 | 187·4 | 61·5 | 5·49 | 5·25 | 1·8394 | 23·85 | 187·8 |
| | | | | | | | | | | Mean | 187·3 |

**87.** n-*Propyl iodide* (Method 1). B. p. 102°/768 mm.; $M$ 170·01; $n_C$ 1·50103, $n_D$ 1·50524, $n_F$ 1·51589, $n_G$ 1·52442. Densities determined: $d_4^{20°}$ 1·7434, $d_4^{42·1°}$ 1·7036, $d_4^{60·9°}$ 1·6693, $d_4^{85·4°}$ 1·6198. Apparatus $A$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 14·5 | 9·14 | 8·90 | 1·7536 | 29·22 | 225·4 | 61·4 | 8·02 | 7·78 | 1·6677 | 24·30 | 226·5 |
| 25·2 | 8·98 | 8·74 | 1·7338 | 28·37 | 226·3 | 85·2 | 7·36 | 7·12 | 1·6202 | 21·60 | 226·7 |
| 41·5 | 8·51 | 8·27 | 1·7047 | 26·40 | 226·1 | | | | | Mean | 226·2 |

($P$ 226·0; Karvonen, *loc. cit.*, gives b. p. 101·9°/765·5 mm., $d_4^{20°}$ 1·7471, $n_C$ 1·50123, $n_D$ 1·50546, $n_F$ 1·51611, $n_G$ 1·52513; Lek, *loc. cit.*, gives $d_4^{20°}$ 1·74892; Timmermans and Delcourt, *loc. cit.*, give b. p. 102·5°/760 mm., $d_4^{20°}$ 1·74890, $n_C$ 1·50148, $n_F$ 1·51600; Audsley and Goss, J., 1942, 358, give $d_4^{20°}$ 1·7458, $n_D^{20°}$ 1·5050.)

**87A.** n-*Propyl iodide* (Method 2). B. p. 101°/749 mm.; $n_C$ 1·50175, $n_D$ 1·50599, $n_F$ 1·51665, $n_G$ 1·52496; $R_C$ 28·63, $R_D$ 28·83, $R_F$ 29·35, $R_G$ 29·74; $Mn_D^{20°}$ 256·03. Densities determined: $d_4^{20°}$ 1·7518, $d_4^{42·2°}$ 1·7087, $d_4^{59·7°}$ 1·6758, $d_4^{86·0°}$ 1·6245. Apparatus $A$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 14·5 | 9·26 | 9·02 | 1·7624 | 29·77 | 225·3 | 60·6 | 7·97 | 7·73 | 1·6737 | 24·23 | 226·1 |
| 24·4 | 9·02 | 8·78 | 1·7433 | 28·66 | 225·6 | 87·5 | 7·27 | 7·03 | 1·6216 | 21·35 | 225·9 |
| 41·1 | 8·50 | 8·26 | 1·7108 | 26·46 | 225·4 | | | | | Mean | 225·8 |

**88.** iso*Propyl iodide* (Method 1). B. p. 89°/762 mm.; $M$ 170·01; $n_C$ 1·49477, $n_D$ 1·49918, $n_F$ 1·51021, $n_G$ 1·51829. Densities determined: $d_4^{20°}$ 1·7025, $d_4^{41·0°}$ 1·6647, $d_4^{62·0°}$ 1·6228. Apparatus $A$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 16·4 | 8·65 | 8·41 | 1·7092 | 26·92 | 226·6 | 40·9 | 7·96 | 7·72 | 1·6648 | 24·07 | 226·3 |
| 25·0 | 8·32 | 8·08 | 1·6932 | 25·62 | 225·9 | 61·6 | 7·31 | 7·07 | 1·6235 | 21·49 | 225·8 |
| | | | | | | | | | | Mean | 225·9 |

(Timmermans and Delcourt, *loc. cit.*, give b. p. 89·5°/760 mm., $d_4^{20°}$ 1·70416, $n_C$ 1·49473, $n_F$ 1·51026; Audsley and Goss, *loc. cit.*, give $d_4^{20°}$ 1·7043, $n_D$ 1·4991.)

**88A.** iso*Propyl iodide* (Method 2). B. p. 88°/749 mm.; $n_C$ 1·49408, $n_D$ 1·49840, $n_F$ 1·50949, $n_G$ 1·51813; $R_C$ 29·16, $R_D$ 29·38, $R_F$ 29·93, $R_G$ 30·35; $Mn_D^{20°}$ 254·74. Densities determined: $d_4^{20°}$ 1·6795, $d_4^{42·9°}$ 1·6507, $d_4^{60·7°}$ 1·6131. Apparatus $A$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 24·5 | 8·50 | 8·26 | 1·6882 | 26·11 | 227·6 | 61·2 | 7·57 | 7·33 | 1·6121 | 22·13 | 229·1 |
| 41·6 | 8·05 | 7·81 | 1·6534 | 24·18 | 228·2 | | | | | Mean | 228·3 |

**89.** n-*Butyl iodide* (Method 1). B. p. 129°/756 mm.; $M$ 184·03; $n_C$ 1·49589, $n_D$ 1·49984, $n_F$ 1·50978, $n_G$ 1·51769. Densities determined: $d_4^{20°}$ 1·6157, $d_4^{41·7°}$ 1·5815, $d_4^{61·5°}$ 1·5492, $d_4^{85·8°}$ 1·5090. Apparatus $A$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 16·9 | 9·92 | 9·68 | 1·6207 | 29·38 | 264·4 | 60·1 | 8·79 | 8·55 | 1·5514 | 24·84 | 264·8 |
| 26·4 | 9·71 | 9·47 | 1·6055 | 28·47 | 264·8 | 86·0 | 8·07 | 7·83 | 1·5088 | 22·12 | 264·6 |
| 41·3 | 9·26 | 9·02 | 1·5821 | 26·72 | 264·5 | | | | | Mean | 264·6 |

($P$ 264·7; Karvonen, *loc. cit.*, gives b. p. 129·3—129·5°/746·5 mm., $d_4^{20°}$ 1·6123, $n_C$ 1·49577, $n_D$ 1·49975, $n_F$ 1·50962, $n_G$ 1·51803; Lek, *loc. cit.*, gives $d_4^{20°}$ 1·61541; Timmermans and Delcourt, *loc. cit.*, give b. p. 130·4°/760 mm., $d_4^{20°}$ 1·61541, $n_C$ 1·49635, $n_D$ 1·50038, $n_F$ 1·51041; Audsley and Goss, *loc. cit.*, give $d_4^{20°}$ 1·6137, $n_D^{20°}$ 1·5000.)

**89A.** n-*Butyl iodide* (Method 2). B. p. 129°/756 mm., $n_C$ 1·49367, $n_D$ 1·49758, $n_F$ 1·50738, $n_G$ 1·51520; $R_C$ 33·48, $R_D$ 33·70, $R_F$ 34·26, $R_G$ 34·79; $Mn_D^{20°}$ 275·60. Densities determined: $d_4^{20°}$ 1·5995, $d_4^{41·5°}$ 1·5619, $d_4^{60·8°}$ 1·5317, $d_4^{86·5°}$ 1·4875. Apparatus $A$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 12·8 | 10·04 | 9·80 | 1·6117 | 29·58 | 266·3 | 60·6 | 8·83 | 8·59 | 1·5320 | 24·64 | 267·6 |
| 22·9 | 9·74 | 9·50 | 1·5944 | 28·36 | 266·4 | 87·8 | 8·06 | 7·82 | 1·4853 | 21·75 | 267·6 |
| 41·0 | 9·32 | 9·08 | 1·5628 | 26·57 | 267·4 | | | | | Mean | 267·2 |

**90.** sec.-*Butyl iodide* (Method 1). B. p. 117·5—118°/750 mm.; $M$ 184·03; $n_C$ 1·49497, $n_D$ 1·49909, $n_F$ 1·50946, $n_G$ 1·51779. Densities determined: $d_4^{20°}$ 1·5920, $d_4^{40·1°}$ 1·5595, $d_4^{60·1°}$ 1·5266, $d_4^{85·5°}$ 1·4838. Apparatus $A$.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 17·3 | 7·49 | 7·25 | 1·5964 | 28·58 | 266·5 | 61·3 | 6·59 | 6·35 | 1·5246 | 23·91 | 267·0 |
| 25·9 | 7·26 | 7·02 | 1·5824 | 27·43 | 266·2 | 87·5 | 6·00 | 5·76 | 1·4806 | 21·06 | 266·7 |
| 41·9 | 6·98 | 6·74 | 1·5566 | 25·91 | 266·7 | | | | | Mean | 266·6 |

(Lek, *loc. cit.*, gives $d_4^{20°}$ 1·59806; Timmermans and Delcourt, *loc. cit.*, give b. p. 120·0°/760 mm., $d_4^{20°}$ 1·59754, $n_C$ 1·49596, $n_D$ 1·50010, $n_F$ 1·51054, $n_G$ 1·51940, $P$ 266·1; Audsley and Goss, *loc. cit.*, give $d_4^{20°}$ 1·5984, $n_D^{20°}$ 1·5000.)

**91.** iso*Butyl iodide* (Method 1). B. p. 119·5°/771 mm.; *M* 184·03; $n_C$ 1·49195, $n_D$ 1·49588, $n_F$ 1·50571, $n_G$ 1·51357. Densities determined: $d_4^{20°}$ 1·6017, $d_4^{42·6°}$ 1·5641, $d_4^{62·5°}$ 1·5305, $d_0^{80·5°}$ 1·4898. Apparatus *D*.

| *t.* | *h.* | *H.* | $d_4^{t°}$. | *γ.* | *P.* | *t.* | *h.* | *H.* | $d_4^{t°}$. | *γ.* | *P.* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 17·5 | 7·44 | 7·20 | 1·6059 | 28·55 | 264·9 | 60·3 | 6·52 | 6·28 | 1·5342 | 23·79 | 264·9 |
| 25·4 | 7·21 | 6·97 | 1·5928 | 27·42 | 264·4 | 85·3 | 5·98 | 5·74 | 1·4918 | 21·15 | 264·9 |
| 41·3 | 6·90 | 6·66 | 1·5663 | 25·76 | 264·7 | | | | | Mean | 264·7 |

(Timmermans and Delcourt, *loc. cit.*, give b. p. 120°/760 mm., $d_4^{20°}$ 1·60346, $n_C$ 1·49238, $n_F$ 1·50630, *P* 264·0; Audsley and Goss, *loc. cit.*, give $d_4^{20°}$ 1·6038, $n_D^{20°}$ 1·4961.)

**92.** n-*Amyl iodide* (Method 1). B. p. 154·5°/761 mm. (very slight decomp.), followed by 52°/20 mm.; *M* 198·06; $n_C$ 1·49171, $n_D$ 1·49540, $n_F$ 1·50474, $n_G$ 1·51222. Densities determined: $d_4^{20°}$ 1·5118, $d_4^{41·1°}$ 1·4827, $d_4^{61·4°}$ 1·4541, $d_4^{86·9°}$ 1·4163. Apparatus *A*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 20·5 | 10·62 | 10·38 | 1·5111 | 29·37 | 305·1 | 61·3 | 9·49 | 9·25 | 1·4542 | 25·19 | 305·1 |
| 21·0 | 10·57 | 10·33 | 1·5104 | 29·22 | 304·9 | 87·2 | 8·75 | 8·51 | 1·4159 | 22·56 | 304·9 |
| 42·0 | 10·04 | 9·80 | 1·4815 | 27·19 | 305·3 | | | | | Mean | 305·1 |

(Karvonen, *loc. cit.*, gives b. p. 153·2—153·5°/743 mm., $d_4^{20°}$ 1·5095, $n_C$ 1·49174, $n_D$ 1·49548, $n_F$ 1·50485, $n_G$ 1·51277; Audsley and Goss, *loc. cit.*, give $d_4^{20°}$ 1·5108, $n_D^{20°}$ 1·4965.)

**92A.** n-*Amyl iodide* (Method 2). B. p. 155°/766 mm., followed by 42°/10 mm.; $n_C$ 1·49229, $n_D$ 1·49607, $n_F$ 1·50548, $n_G$ 1·51286; $R_C$ 38·11, $R_D$ 38·27, $R_F$ 38·88, $R_G$ 39·36; $Mn_D^{20°}$ 296·32. Densities determined: $d_4^{20°}$ 1·5122, $d_4^{41·5°}$ 1·4807, $d_4^{62·2°}$ 1·4503, $d_4^{86·9°}$ 1·4146. Apparatus *A*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 25·5 | 10·42 | 10·18 | 1·5041 | 28·67 | 304·7 | 62·2 | 9·34 | 9·10 | 1·4503 | 24·72 | 304·5 |
| 41·9 | 9·94 | 9·70 | 1·4801 | 26·88 | 304·7 | 86·7 | 8·70 | 8·46 | 1·4149 | 22·41 | 304·6 |
| | | | | | | | | | | Mean | 304·6 |

**93.** iso*Amyl iodide* (Method 1, from fermentation alcohol). B. p. 147·5°/768 mm.; *M* 198·06; $n_C$ 1·48896, $n_D$ 1·49269, $n_F$ 1·50201, $n_G$ 1·50934. Densities determined: $d_4^{20°}$ 1·5025, $d_4^{43·0°}$ 1·4709, $d_4^{61·5°}$ 1·4443, $d_4^{86·3°}$ 1·4071. Apparatus *A*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 25·0 | 9·98 | 9·74 | 1·4955 | 27·28 | 302·7 | 61·3 | 9·02 | 8·78 | 1·4446 | 23·75 | 302·7 |
| 42·1 | 9·56 | 9·32 | 1·4722 | 25·69 | 302·9 | 87·0 | 8·32 | 8·08 | 1·4061 | 21·27 | 302·5 |
| | | | | | | | | | | Mean | 302·7 |

**93A.** iso*Amyl iodide* (Method 1, from synthetic alcohol). B. p. 147·5°/763 mm.; $n_C$ 1·49024, $n_D$ 1·49394, $n_F$ 1·50331, $n_G$ 1·51079; $R_C$ 37·96, $R_D$ 38·20, $R_F$ 38·81, $R_G$ 39·30; $Mn_D^{20°}$ 295·88. Densities determined: $d_4^{20°}$ 1·5092, $d_4^{40·4°}$ 1·4807, $d_4^{61·4°}$ 1·4504, $d_4^{86·5°}$ 1·4129. Apparatus *D*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 21·4 | 7·88 | 7·64 | 1·5072 | 28·40 | 303·5 | 61·1 | 7·15 | 6·91 | 1·4501 | 24·74 | 304·6 |
| 40·6 | 7·54 | 7·30 | 1·4805 | 26·69 | 304·1 | 86·5 | 6·68 | 6·44 | 1·4129 | 22·47 | 305·2 |
| | | | | | | | | | | Mean | 304·3 |

**94.** *γ-Iodopentane* (Method 1). B. p. 141·5—142·5°/773 mm. (very slight decomp.), followed by 41·5°/17 mm.; *M* 198·06; $n_C$ 1·49394, $n_D$ 1·49781, $n_F$ 1·50763, $n_G$ 1·51573. Densities determined: $d_4^{20°}$ 1·5106, $d_4^{41·5°}$ 1·4809, $d_4^{62·4°}$ 1·4504, $d_4^{86·5°}$ 1·4148. Apparatus *A*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 16·9 | 10·41 | 10·17 | 1·5150 | 28·85 | 303·0 | 61·9 | 9·00 | 8·76 | 1·4511 | 23·80 | 301·5 |
| 25·1 | 10·18 | 9·94 | 1·5034 | 27·98 | 302·4 | 97·3 | 8·38 | 8·14 | 1·4137 | 21·55 | 301·9 |
| 41·5 | 9·57 | 9·33 | 1·4809 | 25·87 | 301·6 | | | | | Mean | 302·9 |

(Audsley and Goss, *loc. cit.*, give $d_4^{20°}$ 1·5128, $n_D^{20°}$ 1·4979.)

**95.** *β-Iodopentane* (Method 1). B. p. 141—142°/762 mm. (very slight decomp.), followed by 44·5°/20 mm.; *M* 198·06; $n_C$ 1·49222, $n_D$ 1·49611, $n_F$ 1·50590, $n_G$ 1·51359. Densities determined: $d_4^{20°}$ 1·5096, $d_4^{41·5°}$ 1·4785, $d_4^{60·5°}$ 1·4503, $d_4^{86·8°}$ 1·4114. Apparatus *A*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 17·5 | 10·30 | 10·06 | 1·5133 | 28·51 | 302·4 | 60·2 | 9·00 | 8·76 | 1·4507 | 23·80 | 301·5 |
| 41·2 | 9·48 | 9·24 | 1·4789 | 25·59 | 301·2 | 85·3 | 8·42 | 8·18 | 1·4133 | 21·65 | 302·3 |
| | | | | | | | | | | Mean | 301·8 |

(Audsley and Goss, *loc. cit.*, give $d_4^{20°}$ 1·5020, $n_D^{20°}$ 1·4960.)

**96.** n-*Hexyl iodide* (Method 1). B. p. 180°/774 mm. (very slight decomp.), followed by 45·5°/4 mm.; *M* 212·08; $n_C$ 1·48905, $n_D$ 1·49264, $n_F$ 1·50160, $n_G$ 1·50862. Densities determined: $d_4^{20°}$ 1·4367, $d_4^{41·4°}$ 1·4091, $d_4^{61·6°}$ 1·3826, $d_4^{86·1°}$ 1·3504. Apparatus *D*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 18·3 | 8·70 | 8·46 | 1·4389 | 30·06 | 345·1 | 62·1 | 7·79 | 7·55 | 1·3820 | 25·77 | 345·8 |
| 24·1 | 8·62 | 8·38 | 1·4314 | 29·62 | 345·7 | 85·6 | 7·31 | 7·07 | 1·3511 | 23·59 | 345·9 |
| 41·7 | 8·30 | 8·06 | 1·4087 | 28·04 | 346·4 | | | | | Mean | 345·8 |

(*P* 344·1; Karvonen, *loc. cit.*, gives b. p. 177°/743·7 mm., $d_4^{20°}$ 1·4387, $n_C$ 1·48929, $n_D$ 1·49290, $n_F$ 1·50183, $n_G$ 1·50941; Lek, *loc. cit.*, gives b. p. 180·20°/760 mm., $d_4^{20°}$ 1·43919, $n_C$ 1·48924, $n_F$ 1·50185; Audsley and Goss, *loc. cit.*, give $d_4^{20°}$ 1·4329, $n_D^{20°}$ 1·4930.)

**97.** n-*Heptyl iodide* (Method 1). B. p. 202°/774 mm. (very slight decomp.), followed by 62·5°/3·5 mm.; *M* 226·11; $n_C$ 1·48628, $n_D$ 1·48974, $n_F$ 1·49832, $n_G$ 1·50509. Densities determined: $d_4^{20°}$ 1·3734, $d_4^{41·0°}$ 1·3487, $d_4^{61·1°}$ 1·3248, $d_4^{85·7°}$ 1·2943. Apparatus *D*.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 18·6 | 9·24 | 9·00 | 1·3751 | 30·56 | 386·6 | 61·6 | 8·29 | 8·05 | 1·3242 | 26·33 | 386·8 |
| 20·2 | 9·15 | 8·91 | 1·3732 | 30·22 | 386·1 | 88·3 | 7·75 | 7·51 | 1·2913 | 23·95 | 387·4 |
| 41·0 | 8·68 | 8·44 | 1·3487 | 28·11 | 386·0 | | | | | Mean | 386·6 |

(*P* 384·5; Deffet, *loc. cit.*, gives b. p. 204°/760 mm., $d_4^{20°}$ 1·37949, $n_C$ 1·48699, $n_F$ 1·49916, $n_G$ 1·50567; Lek, *loc. cit.*, gives $d_4^{20°}$ 1·37961; Audsley and Goss, *loc. cit.*, give $d_4^{20°}$ 1·3792, $n_D^{20°}$ 1·4909.)

**98.** n-*Octyl iodide* (Method 1). B. p. 221—221·5°/752 mm. (very slight decomp.), followed by 86·5°/5 mm.; *M* 240·14; $n_C$ 1·48554, $n_D$ 1·48892, $n_F$ 1·49731, $n_G$ 1·50385. Densities determined: $d_4^{20°}$ 1·3297, $d_4^{41·5°}$ 1·3061, $d_4^{61·6°}$ 1·2833, $d_4^{86·5°}$ 1·2549. Apparatus *D*.

| *t*. | *h*. | *H*. | $d_4^t$. | $\gamma$. | *P*. | *t*. | *h*. | *H*. | $d_4^t$. | $\gamma$. | *P*. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 21·0 | 9·58 | 9·34 | 1·3286 | 30·65 | 425·3 | 61·0 | 8·70 | 8·46 | 1·2840 | 26·83 | 425·6 |
| 42·4 | 9·11 | 8·87 | 1·3051 | 28·59 | 425·5 | 86·9 | 8·19 | 7·95 | 1·2545 | 24·63 | 426·4 |
| | | | | | | | | | | Mean | 425·7 |

(Deffet, *loc. cit.*, gives b. p. 225·5°/760 mm., $d_4^{20°}$ 1·33008, $n_C^{20°}$ 1·48514, $n_F$ 1·49688, $n_G$ 1·50363; Audsley and Goss, *loc. cit.*, give $d_4^{20°}$ 1·3295, $n_D^{20°}$ 1·4890.)

The author's thanks are tendered to Imperial Chemical Industries, Ltd., for the liberal grants which have defrayed most of the heavy cost of the research.

WOOLWICH POLYTECHNIC, LONDON, S.E. 18. [*Received, September 20th*, 1943.]

---

## 170. *Transport Numbers of Nitric Acid in Water at 25° from E.M.F. Measurements.*

By H. I. STONEHILL.

The cation transport numbers ($t_+$) of aqueous solutions of nitric acid ($c$ = 0·001 to 0·2 mol./l.) have been determined by combining activity-coefficient data with measurement of the E.M.F. of concentration cells with transport, quinhydrone electrodes being used. The results are compatible with the theoretical limiting value and limiting slope of the $t_+$–$\sqrt{c}$ curve, agree with the Jones–Dole and the Longsworth equation, but not with the Owen equation, and indicate that, up to 0·2 mol./l., the hydrogen ion mobilities in nitric and hydrochloric acids at the same concentration are equal; the nitrate ion mobilities of potassium nitrate (up to $c$ = 0·2) and of silver nitrate (up to $c$ = 0·1) are, however, lower than those of nitric acid.

THE only transport-number data reported for aqueous nitric acid are those, almost exclusively from "International Critical Tables" (1929, **6**, 310), quoted in Table I. These values of $t_+$ (cationic transport number) are plotted against $\sqrt{c}$ in Fig. 1, in which are also shown the straight lines drawn through the theoretical limiting

TABLE I.

*Cation Transport Numbers of Nitric Acid in Water.*

| $c$ (concn., mol./l.) | 0·005 | 0·01 | 0·02 | 0·05 | 0·1 | 0·2 |
|---|---|---|---|---|---|---|
| $t_+$ at 25° (moving boundary) | — | 0·838 | 0·838 | 0·840 | 0·844 * | 0·849 |
| $t_+$ at 18° (moving boundary) | — | — | 0·846 | — | 0·855 | — |
| $t_+$ at 20° (gravimetric) | 0·839 | 0·840 | 0·841 | 0·844 | — | — |

* MacInnes and Cowperthwaite (*Trans. Faraday Soc.*, 1927, **23**, 400) give 0·8441.

values $t_+^0$ (for $c$ = 0), with slopes equal to the limiting slopes given by Longsworth's equation (*J. Amer. Chem. Soc.*, 1932, **54**, 2741; 1935, **57**, 1185)

$$\lim_{c\to 0} dt_+/d\sqrt{c} = \beta(2t_+^0 - 1)/\Lambda^0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The value of β, one of the constants in Onsager's conductivity equation (*Physikal. Z.*, 1926, **27**, 388; 1927, **28**, 277)

$$\Lambda' = \Lambda^0 - (\alpha\Lambda^0 + 2\beta)\sqrt{c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

is taken as 29·93 in water at 25°. The values of $t_+^0$ were obtained from the relation

$$t_+^0 = \lambda_+^0/(\lambda_+^0 + \lambda_-^0) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and are listed, together with the necessary limiting cationic and anionic mobilities ($\lambda_{H^+}^0$ and $\lambda_{NO_3^-}^0$), in Table II. It appears from Fig. 1 that there is little tendency for the moving-boundary transport numbers at 18° to

TABLE II.

*Limiting Ionic Mobilities, Cation Transport Numbers, and Slopes.*

| Temp. | $\lambda_{H^+}^0$. | $\lambda_{NO_3^-}^0$. | $t_+^0$. | $\beta$. | $\lim_{c\to 0} dt_+/d\sqrt{c}$. |
|---|---|---|---|---|---|
| 18° | 315·2 (*a*) | 61·62 (*a*) | 0·8365 | 25·17 | 0·04495 |
| 20 | 325·1 (*b*) | 64·42 (*b*) | 0·8346 | 26·52 | 0·04557 |
| 25 | 349·72 (*c*) | 71·42 (*c*) | 0·8304 | 29·93 | 0·04696 |

(*a*) "International Critical Tables," 1929, **6**, 230; (*b*) interpolated; (*c*) MacInnes, Shedlovsky, and Longsworth, *J. Amer. Chem.* Soc., 1932, **54**, 2758.

merge into the theoretical limiting slope as $c$ decreases; the agreement is better for the gravimetric values at 20°, and also for the moving-boundary values at 25°, except for the lowest two concentrations in each case. The discrepancies are in the wrong direction and far too great to be ascribed to the omission of the correction for the conductivity of the solvent (Longsworth, *loc. cit.*, 1932); they may possibly be due to the experimental

difficulties inherent in the gravimetric and the moving-boundary method (*idem, ibid.*, 1935, **57**, 1185) at low concentrations. It is clear that further independent measurements are desirable.

Hitherto no transport numbers for nitric acid derived from E.M.F. measurements have been reported. This may be because the usual E.M.F. method necessitates the measurement of cells both with and without transport; the former demands two identical electrodes, both reversible to the same ion, either $H^+$ or $NO_3^-$, and the latter a pair of non-identical electrodes, one reversible to $H^+$, the other to $NO_3^-$. Since, however, accurate activity-coefficient data for nitric acid are available (Hartmann and Rosenfeld, *Z. physikal. Chem.*, 1933, **164**, 377), the second type of cell may be dispensed with. In the absence of any electrode reversible to

FIG. 1.

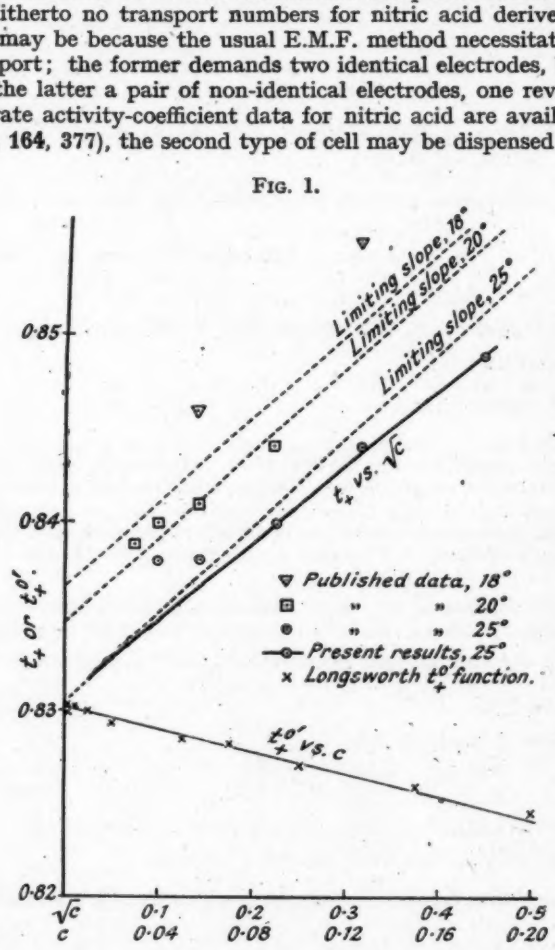
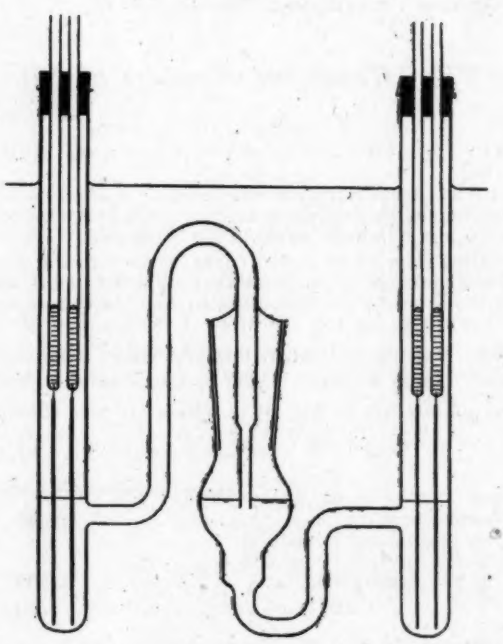



FIG. 2.



$NO_3^-$, there now remains the necessity for an electrode, reversible to $H^+$, which will function in nitric acid. The hydrogen electrode itself is useless owing to its reducing action on the acid, but the quinhydrone electrode is applicable up to at least 0·2 mol./l., with a known salt error (Stonehill, *Trans. Faraday Soc.*, 1943, **39**, 67). The method therefore adopted was to measure at 25° the E.M.F. of cells with transport of the type Pt|quinhydrone (satd.), $HNO_3$ ($m'$, fixed)|$HNO_3$ ($m$, variable), quinhydrone (satd.)|Pt, which, after correction for the electrode salt error, is given by

$$E = (2RT/F)\int_{m\gamma}^{m'\gamma'} t_- \mathrm{d} \ln m\gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $m$ and $m'$ are molalities (mols./1000 g. of water), and $\gamma$ and $\gamma'$ are mean ionic activity coefficients corresponding to this concentration scale. By differentiation of (4), we have

$$(F/2RT)\mathrm{d}E/\mathrm{d} \ln m\gamma = t_- = (1 - t_+) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

## EXPERIMENTAL.

The auxiliary apparatus (potentiometer, thermostat, etc.), and the preparation of quinhydrone, stock nitric acid, and cell solutions have already been described (Stonehill, *loc. cit.*). For some preliminary measurements with higher nitric acid concentrations the cell with a ground-glass cap junction (*loc. cit.*) was used; the inner compartment contained the more concentrated of the two acid solutions, and the outside of the inner vessel was rinsed with the more dilute acid solution before assembly of the two compartments; the bubble trap was sealed, and excess of quinhydrone was added to both compartments, which were each provided with a pair of bright gold wire electrodes. The high electrical resistance of the ground-glass junction made it difficult to obtain reliable results for nitric acid concentrations lower than about 0·1 mol./l. Therefore the cell shown in Fig. 2 was used for the main set of measurements, over the concentration range 0·001—0·2 mol./l. This cell consists of two half-cells which connect to form a simple dipping-type liquid junction. The left-hand compartment, while detached from the right-hand section, was filled with the more dilute of the two cell solutions, so that a pendant drop remained at the end of the narrow tube where the liquid junction was to be formed; excess of quinhydrone was added to the test-tube-shaped electrode vessel, and a rubber stopper carrying two bright gold

wire electrodes was fitted into place. The right-hand compartment was then filled with the other solution to about the middle of the bulb below the ground-glass joint, quinhydrone added, and a stopper with two gold wire electrodes fitted; the cell was then assembled, so that at the liquid junction the denser solution was below the other. The ground-glass joint was lubricated with light vacuum grease to resist leakage of thermostat liquid (kerosene) into the cell. It was necessary to ensure that no quinhydrone diffused into the liquid junction region, otherwise variable results were obtained. The cell was also tested for interdiffusion of the solutions by placing potassium permanganate solution on one side and water on the other; no colour diffused into the neighbourhood of the water-filled electrode vessel in 48 hrs. Cells were measured at 25° ± 0·01° for 6—12 hrs. Equilibrium ensued in about 2—3 hrs. for intermediate concentrations, rather longer for the more dilute, and shorter for the more concentrated solutions; in the latter, however, rapid drifts were observed after about 2 hrs., due to interaction of quinhydrone and nitric acid (Stonehill, *loc. cit.*); for this reason, no reliable values could be obtained for concentrations above about 0·2 mol./l. Duplicate cells were measured in all cases, and agreed within 0·03 mv. or rather better for the more dilute solutions; the two electrodes in each half-cell generally agreed to within 0·01—0·03 mv. With a given pair of solutions, both the old and the new cell gave the same results.

*Results.*—The values of the nitric acid concentration ($c$ mols./l. of solution, or $m$ mols./kg. of water), the observed E.M.F. ($E_{obs.}$), and log $\gamma$ are given in Table III. The fixed solution in one half of the cell had concentration $c' = 0{\cdot}1038$.

TABLE III.

*Experimental E.M.F. Results.**

| $c$. | $m$. | $-\log\gamma$. | $E_{obs.}$. | $\Delta E$. | $E_{corr.}$. | $E'$. |
|---|---|---|---|---|---|---|
| 0·2040 | 0·2058 | 0·1242 | 4·56 | 0·54 | 5·10 | 21·36 |
| 0·1530 | 0·1542 | 0·1158 | 2·74 | 0·27 | 3·01 | 21·62 |
| 0·1020 | 0·1027 | 0·1034 | 0·00 | 0·00 | 0·00 | 21·90 |
| 0·09184 | 0·09236 | 0·1001 | − 0·78 | −0·05 | − 0·83 | 21·93 |
| 0·08164 | 0·08209 | 0·0966 | − 1·55 | −0·11 | − 1·66 | 22·05 |
| 0·06123 | 0·06152 | 0·0879 | − 3·69 | −0·22 | − 3·91 | 22·14 |
| 0·05103 | 0·05126 | 0·0825 | − 4·99 | −0·27 | − 5·26 | 22·27 |
| 0·04082 | 0·04099 | 0·0762 | − 6·71 | −0·32 | − 7·03 | 22·32 |
| 0·03061 | 0·03073 | 0·0685 | − 8·90 | −0·38 | − 9·28 | 22·43 |
| 0·02041 | 0·02048 | 0·0584 | −12·00 | −0·43 | −12·43 | 22·61 |
| 0·01021 | 0·01024 | 0·0439 | −17·53 | −0·49 | −18·02 | 22·77 |
| 0·005102 | 0·005118 | 0·0324 | −23·17 | −0·51 | −23·68 | 22·92 |
| 0·002042 | 0·002048 | 0·0212 | −30·81 | −0·53 | −31·34 | 23·02 |
| 0·001021 | 0·001024 | 0·0154 | −36·70 | −0·53 | −37·23 | 23·04 |

* All values of $E$ in millivolts, and with European sign convention (Stonehill, *loc. cit.*).

Values of $m$ for a given $c$ were obtained from the equation (Stonehill, *loc. cit.*, p. 72)

$$m/c = 1{\cdot}00298 + 0{\cdot}029855c + 0{\cdot}001142c^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and values of $\gamma$ for a given $m$ were obtained from a large-scale graph of $\gamma$ against $\sqrt{m}$ plotted from the data of Hartmann and Rosenfeld (*loc. cit.*). The correction for the salt error of the quinhydrone electrodes was obtained by adding

$$\Delta E = (c' - c) \times (0{\cdot}00529 \pm 0{\cdot}00005)\text{v.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

to $E_{obs.}$, thus giving $E_{corr.}$. The probable error in the second factor in equation (7) causes a maximum uncertainty of 0·005 mv. in $E_{corr.}$, which is less than the experimental error.

To carry out the differentiation indicated in (5), the slope of the graph to be plotted was first reduced by subtracting $(RT/F)\, t^0_- \ln (m\gamma) = 20{\cdot}058 \log (m\gamma)$ (in mv.) from $E_{corr.}$, giving $E'$, so that instead of equation (5) there now remained

$$\frac{F}{2RT}\frac{dE'}{d\ln m\gamma} = \frac{1}{118{\cdot}3}\frac{dE'}{d\log m\gamma} = \frac{d(E_{corr.} - 20{\cdot}058\log m\gamma)}{118{\cdot}3\, d\log m\gamma} = t_- - t^0_- = t^0_+ - t_+ \quad . \quad . \quad . \quad . \quad (8)$$

where $E_{corr.}$ and $E'$ are in mv. Thus the values of $E'$, given in Table III, were plotted against log $m\gamma$, and the slope of the smooth curve drawn through the points so obtained was determined at intervals of 0·1 in log $m\gamma$ by the use of Rutledge's derivative function (*Physical Rev.*, 1932, **40**, 262); this method is equivalent to fitting a fourth-degree equation to successive sets of five equispaced ordinates at various positions along the curve. From these slopes values of $t_+$ were obtained by using equation (8). These preliminary $t_+$ values were then plotted against $E'$, and smoothed by drawing a smooth curve as evenly as possible through the plotted points. The average deviation of the latter from the smoothed curve was 0·0005 (compare the average deviation of 0·005 in the similar treatment of the results of Harned and Dreby, *J. Amer. Chem. Soc.*, 1939, **61**, 3113, for hydrochloric acid in water). Smoothed values of $t_+$ for values of $E'$ corresponding to round values of $c$ (read off a graph of $E'$ against $\sqrt{c}$) were read off; these are listed in Table IV, col. 3. Account being

TABLE IV.

*Experimental Cation Transport Numbers for Nitric Acid at 25°, and Various Extrapolation Functions.*

| $c$. | $\sqrt{c}$. | $t_+$ (expt.). | $1/(1 + t_+)$. | $t^0_+$. | $t_+$ (eq. 12). |
|---|---|---|---|---|---|
| 0·001 | 0·03162 | 0·8321 | 0·54584 | 0·8303 | 0·8318 |
| 0·002 | 0·04472 | 0·8327 | 0·54564 | 0·8300 | 0·8324 |
| 0·005 | 0·07071 | 0·8336 | 0·54539 | 0·8302 | 0·8335 |
| 0·01 | 0·1000 | 0·8348 | 0·54503 | 0·8300 | 0·8346 |
| 0·02 | 0·1414 | 0·8366 | 0·54450 | 0·8294 | 0·8360 |
| 0·05 | 0·2236 | 0·8400 | 0·54348 | 0·8286 | 0·8384 |
| 0·07 | 0·2450 | 0·8408 | 0·54324 | 0·8283 | 0·8386 |
| 0·10 | 0·3162 | 0·8437 | 0·54241 | 0·8271 | 0·8402 |
| 0·15 | 0·3873 | 0·8466 | 0·54154 | 0·8259 | 0·8410 |
| 0·20 | 0·4472 | 0·8492 | 0·54078 | 0·8246 | 0·8413 |

taken of the average deviation in the smoothing process, and of the average experimental error of 0·02 mv. in $E'$, which produces by the Rutledge method an average error in $t_+$ of 0·0008, the probable error in $t_+$ is of the order $\pm$0·0008. The correction for solvent conductivity is negligible, being $-$0·0004 at $c = 0·001$, and less for higher concentrations.

## Discussion.

The final values of $t_+$ are plotted against $\sqrt{c}$ in Fig. 1 as an unbroken curve. This merges into the limiting slope and limiting value $t_+^0 = 0·8304$ satisfactorily, indicating that the present results at concentrations below $c = 0·02$ are better than the values from "International Critical Tables." Above $c = 0·02$, the latter values and the present ones agree quite well within the uncertainty limits of $\pm$0·001.

Jones and Dole (*J. Amer. Chem. Soc.*, 1929, **51**, 1073) proposed the equation

$$t_+ = A/(1 + B\sqrt{c}) - 1 \text{ or } 1/(1 + t_+) = 1/A + B\sqrt{c}/A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

for extrapolating $t_+$ against $\sqrt{c}$ in order to obtain $t_+^0$. If this equation holds, a plot of $1/(1 + t_+)$ against $\sqrt{c}$ should be linear. Values of $1/(1 + t_+)$ from the present results are given in Table IV, col. 4; when plotted against $\sqrt{c}$ they lie fairly well on a straight line which upon extrapolation gives an intercept $1/A = 1/(1 + t_+^0) = 0·54624$, and thus $t_+^0 = 0·8307$. The agreement with the known value $t_+^0 = 0·8304$ is gratifying though perhaps fortuitous in view of the probable uncertainty in the $t_+$ values.

Longsworth (*loc. cit.*, 1932) proposed the equation

$$t_+ = t_+^0 + (2t_+^0 - 1)\beta\sqrt{c}/\Lambda' + Ac(1 + 2\beta\sqrt{c}/\Lambda') \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where $A$ is an empirical parameter, and $\Lambda'$ and $\beta$ are connected by Onsager's equation (2), in which $\alpha$ and $\beta$ are constants having the respective values 0·2277 and 29·93 in water at 25°. From equation (10) Longsworth derived an extrapolation function

$$t_+^{0'} = (t_+\Lambda' + \beta\sqrt{c})/(\Lambda' + 2\beta\sqrt{c}) = t_+^0 + Ac \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

which, when plotted against $c$, should give a straight line extrapolating to $t_+^0$. Values of $t_+^{0'}$ calculated from the present $t_+$ values are listed in Table IV, col. 5, and plotted against $c$ in Fig. 1; apart from one or two values, they lie on a straight line with slope $A = -0·030$ and intercept $t_+^0 = 0·8302$. The agreement with the known value $t_+^0 = 0·8304$ is again better than might have been expected.

Owen (*J. Amer. Chem. Soc.*, 1935, **57**, 2441) proposed the equation

$$t_+ = t_+^0 + (2t_+^0 - 1)\beta\sqrt{c}[1 - (1 - \alpha\sqrt{c})\sqrt{2c}]/\Lambda' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

which is equivalent to equation (10) if we put

$$A = -\beta\sqrt{2}(2t_+^0 - 1)/\Lambda^0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

the quantities $\Lambda^0$, $\Lambda'$, $\alpha$, and $\beta$ having the same significance as in equations (2) and (10). Owen's equation has the advantage that only $t_+^0$, without any arbitrary parameter, is required in order to calculate $t_+$ values. The equation was tested by calculating values of $t_+$ from it for various round concentrations. The values obtained are given in Table IV, col. 6, and are seen to diverge increasingly from the present values as $c$ increases above 0·01. Owen's equation thus fails for nitric acid. This could be seen at once by comparing the experimental value of $A$, *viz.*, $-$0·030, with the value required by equation (13), *viz.*, $-$0·066.

MacInnes and Cowperthwaite (*Trans. Faraday Soc.*, 1927, **23**, 400) showed that at concentration $c =$ 0·1 mol./l. the value of $t_+ \Lambda = \lambda_{H^+}$ was approximately the same for both hydrochloric and nitric acid in water at 25°. By using the present values of $t_+$ for nitric acid and more recent values of the equivalent conductivities ($\Lambda$) of both acids and of $t_+$ for hydrochloric acid, the validity of this relation for concentrations up to 0·2 mol./l. was tested. The details are given in Table V. The agreement of the hydrogen-ion mobilities of the two acids

Table V.

*Hydrogen-ion Mobilities in Nitric and Hydrochloric Acids at 25°.*

| $c$. | 0·005. | 0·01. | 0·02. | 0·05. | 0·1. | 0·2. | References. |
|---|---|---|---|---|---|---|---|
| $\Lambda^{HNO_3}$ ..... | 411·2 | 407·3 | 402·8 | 394·0 | 386·0 | 376·1 | I.C.T., 1929, **6**, 242 |
| $t_+^{HNO_3}$ ..... | 0·8334 | 0·8348 | 0·8366 | 0·8398 | 0·8437 | 0·8488 | Present results. |
| $\lambda_{H^+}^{HNO_3}$ ..... | 342·6 | 340·0 | 337·0 | 330·9 | 325·7 | 319·2 | |
| $\Lambda^{HCl}$ ..... | 415·7 | 411·9 | 407·1 | 399·0 | 391·2 | 381·3 | I.C.T., 1929, **6**, 242; Shedlovsky, *J. Amer. Chem. Soc.*, 1932, **54**, 1411 |
| $t_+^{HCl}$ ..... | 0·8239 | 0·8251 | 0·8266 | 0·8292 | 0·8314 | 0·8337 | Longsworth (*locc. cit.*) |
| $\lambda_{H^+}^{HCl}$ ..... | 342·5 | 339·9 | 336·5 | 330·9 | 325·2 | 317·9 | |

is reasonably good up to $c = 0·1$, and possibly up to $c = 0·2$ if allowance is made for the uncertainty in the values of $t_+$ for nitric acid and the unknown probable error in the values of $\Lambda$ for nitric acid, which are not so precise as those for hydrochloric acid. It appears, then, that Kohlrausch's law of independent ion mobilities holds here up to $c = 0·2$, and that up to this concentration at least nitric acid must be regarded as completely

dissociated if hydrochloric acid is assumed to be so. A similar comparison of values of $\lambda_{NO_3^-}$ in nitric acid, potassium nitrate, and silver nitrate at 25° (Table VI) amplifies the results for $c = 0{\cdot}1$ obtained by MacInnes and Cowperthwaite (*loc. cit.*), and confirms their conclusion that the two salts are incompletely dissociated.

TABLE VI.

*Nitrate-ion Mobilities in Nitric Acid, Potassium Nitrate, and Silver Nitrate at 25°.*

| $c$. | 0·01. | 0·02. | 0·05. | 0·1. | 0·2. | References. |
|---|---|---|---|---|---|---|
| $\lambda^{HNO_3}_{NO_3^-}$ ..... | 67·3 | 65·8 | 63·1 | 60·3 | 56·9 | See Table V |
| $\Lambda^{KNO_3}$ ..... | 135·8 | 132·4 | 126·8 | 120·4 | 113·3 | Shedlovsky, *loc. cit.*; I.C.T., 1929, **6**, 242 |
| $f^{KNO_3}$ ..... | 0·4916 | 0·4913 | 0·4907 | 0·4897 | 0·4880 | Longsworth, *loc. cit.*, 1935 |
| $\lambda^{KNO_3}_{NO_3^-}$ ..... | 66·8 | 65·1 | 62·2 | 59·0 | 55·3 | |
| $\Lambda^{AgNO_3}$ ..... | 124·72 | 121·37 | 115·20 | 109·10 | — | Shedlovsky, *loc. cit.* |
| $f^{AgNO_3}$ ..... | 0·5352 | 0·5348 | 0·5336 | 0·5318 | — | MacInnes and Cowperthwaite, *Chem. Rev.*, 1932, **11**, 171 |
| $\lambda^{AgNO_3}_{NO_3^-}$ ..... | 66·74 | 64·91 | 61·48 | 58·01 | — | |

The author thanks Mr. J. F. Hill, B.Sc., for valuable help in the arithmetical work, and the Chemical Society for the loan of apparatus.

TECHNICAL COLLEGE, BRADFORD, YORKS. [*Received, October 19th*, 1943.]

## 171. *Aminoacridines: Some Partition and Surface Phenomena.*

By ADRIEN ALBERT, REGINALD GOLDACRE, and ERIC HEYMANN.

In order to obtain data for a closer correlation of physical and biological properties among kationic antiseptics, the oil–water partition coefficients and the air–water surface activities of a number of aminoacridines have been measured. Some correlations between these physical properties and the molecular structure are discussed.

The results suggest that marked oleophilic and surface-active properties are unnecessary for, and if present in high degree are inimical to, the development of good antiseptic properties in this series.

IT has been shown (Albert, Goldacre, and Rubbo, *Nature*, 1941, **147**, 709) that those monoaminoacridines which are most active against bacteria are more strongly ionised and more hydrophilic than those with weakly bacteriostatic properties. To widen the scope of this observation, determination of the distribution of a number of other aminoacridines between olive oil and water has now been made. Further, the surface activity of all these compounds at the air–water interface has been measured, since it may serve as a rough guide to the relative degrees of adsorption at non-water–water interfaces in living material. Apart from a determination of the comparative drop numbers of rivanol and euflavine at various pH values (Michaelis and Hayashi, *Z. Immunforsch.*, 1923, **36**, 518), no investigation of distribution phenomena in the acridine series has yet been made.

Col. A = pH value. Col. B = Approximate percentage ionised. Col. C = Partition coeff., olive oil/water, at 20° ± 5°. Col. D = Depression of surface tension of water at 15° ± 2° by $2{\cdot}5 \times 10^{-4}$ mol./l., in dynes/cm.

| | A. | B. | C. | D. |
|---|---|---|---|---|
| Acridine | | 0·8 | 200 | 2 |
| 1-Aminoacridine | | 0·1 | 1200 | 7 |
| 2-Aminoacridine | | 93 | 5·2 | 0·2 |
| 3-Aminoacridine | | 5 | 90 | 1·5 |
| 4-Aminoacridine | | 11 | 55 | 0 |
| 5-Aminoacridine (mesocrin) | | 100 | 1·2 | 0 |
| 2 : 5-Diaminoacridine | | 100 | 1 | 0 |
| 2 : 7-Diaminoacridine | | 94 | * | 0 |
| 2 : 8-Diaminoacridine (proflavine) | | 100 | 0·7 | 0 |
| 2 : 5-Diamino-7-ethoxyacridine (rivanol) | | 100 | 21 | 12·5 |
| 2 : 8-Diaminoacridine-10-methochloride (euflavine) | 7·0—7·2 | 100 | <0·2 | 0 |
| 2 : 8-Bisdimethylaminoacridine (acridine-orange) | | 100 | 7·3 | 1·5 |
| 2-Aminoacridine-7-sulphonic acid | | 90 | 0·9 | 0 |
| 2-Chloro-5-(δ-diethylamino-α-methyl)butylamino-7-methoxyacridine (atebrin or mepacrine) | | 100 | 31 | 0·2 |
| 5-Methylaminoacridine | | 100 | 12 | 0 |
| 5-Butylaminoacridine | | 100 | 16 | 1·5 |
| 5-*cyclo*Hexylaminoacridine | | 100 | 77 | 2·5 |
| 5-Heptylaminoacridine | | 100 | *ca.* 1000 | 18 |
| 5-Dodecyl- and 5-hexadecyl-aminoacridines | | 100 | * | * |
| 5-Aminoacridine | 10·0 | 40 | 3 | — |
| 3-Aminoacridine | 4·7 | 93 | — | 1·5 |
| 3-Aminoacridine | 2·3 | 100 | — | 0 |
| 5-Butylaminoacridine | 3·6 | 100 | — | 0·5 |
| 5-Heptylaminoacridine | 4·0 | 100 | — | 9 |
| 5-Dodecylaminoacridine | 4·3 | 100 | — | 36 |
| 5-Hexadecylaminoacridine | 4·0 | 100 | — | 26 |
| Rivanol (see above) | 4·6 | 100 | — | 0 |
| 2-*Chloro*-5-*amino*-7-*methoxyacridine* | 4·6 | 100 | — | 1 |

* Solubility difficulties made measurements impossible.

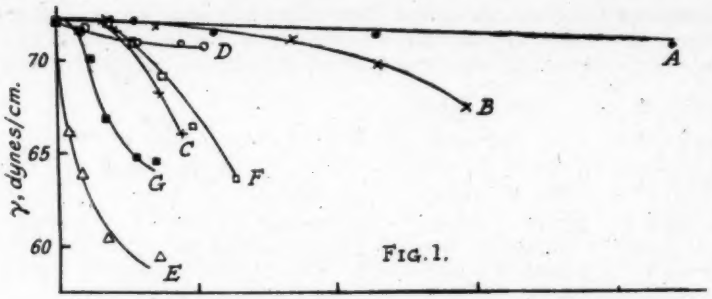



FIG. 1.

*A*. 2-Aminoacridine, pH 7·1.
*B*. Atebrin, pH 7·2.
*C*. Acridine, pH 7·2.
*D*. Acridine-orange, pH 7·0.
*E*. Rivanol, pH 7·0.
*F*. 3-Aminoacridine, pH 7·2.
*G*. 1-Aminoacridine, pH 7·2.

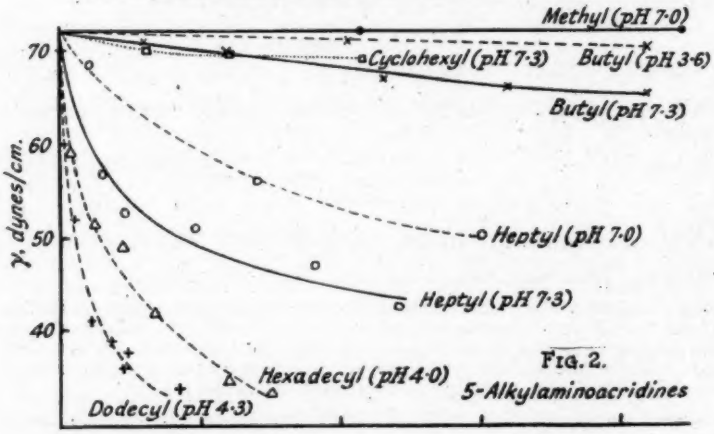



FIG. 2.
5-Alkylaminoacridines

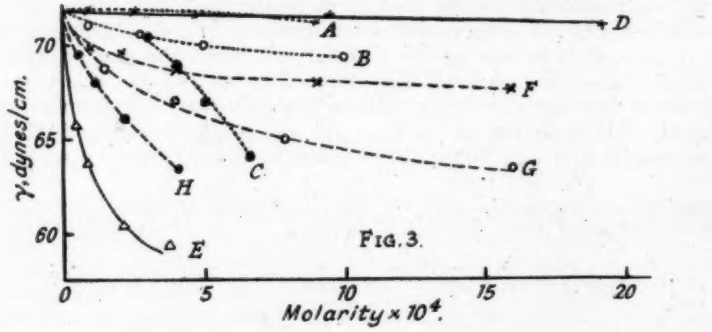



FIG. 3.

*A*. 3-Aminoacridine, pH 2·3.
*B*. 3-Aminoacridine, pH 4·7.
*C*. 3-Aminoacridine, pH 7·2.
*D*. Rivanol, pH 4·6.
*E*. Rivanol, pH 7·0.
*F*. Crystal-violet, pH 4·5.
*G*. Crystal-violet, pH 7·1.
*H*. Crystal-violet, pH 8·4.

*Discussion of Partition Coefficients.*—The partition coefficients oil/water at pH 7 of acridine and the five aminoacridines are seen to be roughly parallel to the amounts of un-ionised bases present. That other factors play some part is suggested by the relatively low value for 5-aminoacridine at pH 10, and it is unlikely that all the undissociated bases are equally oleophilic or all the ions equally hydrophilic. As would be expected, the partition coefficient of an aminoacridine is lowered by addition of another amino-group (*e.g.*, proflavine and 2 : 5-diaminoacridine), but only slightly, since at pH 7 no new ion is formed. Quaternisation of the ring nitrogen above (cf. euflavine) also reduces the coefficient. On the other hand, it is raised by alkylation of a primary amino-group (cf. acridine-orange) and increases with the length of the substituent group until (as with 5-dodecylaminoacridine) the salts, although completely ionised in aqueous solution, have become so oleophilic that they pass from water entirely into the oil. The heightened coefficients of rivanol (I) and the antimalarial atebrin (II) as compared with 5-aminoacridine are attributed to the ethoxy- and the chlorine substituent respectively.

*Discussion of Surface Activities.*—It will be seen from the table that a number of acridine derivatives do not lower the surface tension of water at pH 7, and 2-aminoacridine and atebrin lower it only slightly. The remaining substances show substantial reductions (Figs. 1 and 2), and although the orders of surface activities and partition coefficients do not coincide, these substances have high partition coefficients.

Two important factors that favour surface-activity are feeble ionisation and a relative propinquity of the main centres of hydration to one another so as to create the tendency towards a definite orientation. This concept may serve to explain the high surface activity of acridine and 1-aminoacridine, the lower degrees of activity shown by 2- and 3-aminoacridine, and the absence of this quality in the 4- and the 5-isomeride. The apparent reversal of order of 2- and 3-aminoacridines, as estimated by the propinquity factor, is accounted for

by the much greater degree of ionisation of the former (see table). Some examples are given (Fig. 2 and particularly Fig. 3) of the effect of pH on surface activity. The latter is less in acid solution on account of the increased ionisation (see table), and this accords with the general principle that ions, because of their greater hydration, are adsorbed less strongly at a water boundary than are the corresponding un-ionised molecules.

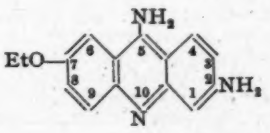
Traube's rule, that the surface tension of water is lowered more strongly as the chain length of an alkyl radical increases, is qualitatively exemplified by the series of 5-alkylaminoacridines (Fig. 2). As the higher homologues have water-insoluble hydrochlorides and phosphates, a series of acetates were measured at pH 4. The apparent reversal of positions of the dodecyl and hexadecyl homologues is connected with the formation of colloidal micelles as indicated by the increasing turbidity of their solutions. Actually, the lower members of this series pass through ultrafilters (prepared according to Bechhold and Gutlohn, *Z. angew. Chem.*, 1924, **37**, 494, from 5% collodion in acetic acid), although there is considerable adsorption on the membrane. The particles of the two higher homologues, however, are completely retained by these filters, whose pore-size can be judged from the fact that they retain most proteins but allow serum albumin to pass.

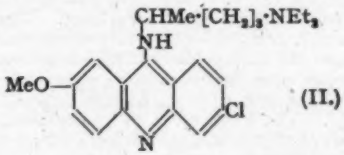
As for the connexion between constitution and surface activity among the more complicated structures, the increased activity of rivanol (I) over 2 : 5-diaminoacridine is attributed to the ethoxy-group, but atebrin (II), which is more oleophilic than (I), is only slightly surface active. Observations on 2-chloro-5-amino-7-methoxyacridine, *i.e.*, atebrin shorn of its side chain, could not be carried out at pH 7 because of solubility difficulties, but at pH 4·6 it was more surface-active than rivanol.

Crystal-violet (*tert.*-dimethylaminotriphenylcarbinol anhydride chloride), which is the most important member of the surface-active triphenylmethane antiseptics, has been included in Fig. 3 for comparison.

Dr. S. D. Rubbo, of Melbourne University, who has been assessing the antiseptic values of these substances, reports that the most antibacterial of the aminoacridines were found among the most hydrophilic members of the above list, *i.e.*, those with partition coefficients of about unity and little or no surface-activity. Rivanol, which is rather oleophilic and yet almost as antibacterial as 5-aminoacridine, was the sole exception. Further, there are indications of a correlation between surface-activity and the depression of bactericidal activity on the addition of red blood cells (cf. Rubbo, Albert, and Maxwell, *Brit. J. Exp. Path.*, 1942, **23**, 69). Phenobarbitone and butanol are instanced as other biologically active substances with an oil/water coefficient of about unity.

(I.)




(II.)

## Experimental.

The percentage ionisation was calculated from both unpublished and published (Albert and Goldacre, this vol., p. 454) figures for p$K_a$ values in dilute alcohols, the p$K_a$ values in water being estimated as approximately 0·5 unit higher.

Neutral olive oil was prepared, following the Argentinian Pharmacopœia, by determining the free acidity of olive oil (B.P. grade) and treating it with sodium carbonate crystals (roughly equal to the weight of fatty acid present) dissolved in ten times their volume of water, the oil being added in 5 successive portions to the alkali at 40° during 2½ hours, with vigorous shaking for 5 mins. after each addition. After 15 hours, the mixture was filtered through dried paper, mixed with a third of its volume of 95% alcohol, and shaken vigorously several times during 24 hours. The oil was separated and heated at 160° for an hour.

Partition coefficients were determined by dissolving the hydrochlorides of each amine (range 0·5—5·0 mg. usually, in regular steps) in phosphate buffer (100 ml., pH 7·0). This was shaken at 25° for 2 hours with sufficient neutral olive oil to extract approximately half the amine, as determined from preliminary experiments. The emulsion was centrifuged, and the aqueous layer compared in a colorimeter with the unextracted solution, which was then diluted to approximately the value found for the extracted solution, and the two solutions were compared again to guard against deviations from Beer's law. In such cases where there was a marked change of colour on acidification, both solutions were then brought to pH 2·5 and compared again. Concordant figures were obtained from the various methods, but some substances, marked with an asterisk in the table, could not be measured because either they were too sparingly soluble in both phases or they were exclusively soluble in one of the phases. The principal difficulty encountered was the matching of so many yellow solutions, an error of up to 10% with this colour being hard to avoid. The method is illustrated by results for 4-aminoacridine :

| | | | | | | |
|---|---|---|---|---|---|---|
| Mg. per 100 ml. ..... | 0·9 | 1·0 | 1·2 | 1·5 | 2·5 | 5·0 |
| Coefficient ..... | 54 | 55 | 56 | 49 | 58 | 57 (average 55) |

No evidence that any compound was associated in the oily layer was found. The values for acridine and 1-aminoacridine were obtained by a slightly different method, as previously described (Albert, Goldacre, and Rubbo, *loc. cit.*), the data previously quoted having been slightly amended by averaging the results of further experiments.

Surface tensions were measured by the ring method, a Cenco–Du Nouy tensiometer being employed. The experimental precautions specified by Harkins and Brown (*J. Amer. Chem. Soc.*, 1919, **41**, 499; also Harkins, Young, and Cheng, *Science*, 1926, **64**, 333; Harkins and Jordan, *J. Amer. Chem. Soc.*, 1930, **52**, 1751) were rigidly observed and the experimental values were corrected by the aid of factors worked out by these investigators. With some compounds (*e.g.*, 2 : 7-diaminoacridine and acridine-orange) difficulties were encountered because of the comparative physical instability of the solution at the pH studied. The majority of the experiments were carried out in phosphate buffer between pH 7·0 and 7·2 as measured by a glass electrode and Cambridge valve potentiometer. The more acid solutions were buffered with citric acid and disodium phosphate according to McIlwaine.

*Materials.*—Acridine, m. p. 110°, was purified by steam distillation. The other substances were prepared and purified according to the following methods: 1-, 2-, 3-, and 4-aminoacridines (Albert and Ritchie, *J. Soc. Chem. Ind.*, 1941, **60**, 120); 5-amino- and 5-chloro-acridine (*idem*, *Organic Syntheses*, 1942, **22**, 5); proflavine (Albert, J., 1941, 121); euflavine (Hall and Powell, *Quart. J. Pharm.*, 1934, **7**, 522); 5-methylaminoacridine (Albert and Ritchie, this vol., p. 454); 2 : 7-diaminoacridine (Aust. Patent, 115,480, 1942, to University of Sydney); 2 : 5-diaminoacridine and 2 : 5-diamino-7-ethoxyacridine (Albert and Gledhill, *J. Soc. Chem. Ind.*, 1942, **61**, 159); 2 : 5-dichloro-7-methoxyacridine and mepacrine (I. G. Farb. Ind., B.P. 1930, 363,392); acridine-orange (Biehringer, *J. pr. Chem.*, 1896, **54**, 243); 2-aminoacridine-7-sulphonic acid (Aarons and Albert, J., 1942, 183); crystal-violet (Kovache, *Ann. Chim.*, 1918, **10**, 247).

*New Compounds.*—*2-Chloro-5-amino-7-methoxyacridine.* 2 : 5-Dichloro-7-methoxyacridine (2·8 g.) and phenol (11 g.) were heated to 70°, and effloresced ammonium carbonate (1·4 g.) added. The mixture was then heated at 120° for 15 mins., cooled, and treated with acetone (30 ml.). The precipitated hydrochloride of 2-chloro-5-amino-7-methoxyacridine was washed with acetone and recrystallised from 1 l. of boiling water; yield, 2·5 g. (85%) of brilliant yellow crystals, m. p. 340° (decomp.), soluble in about 290 parts of hot and 2,000 parts of cold water with a green fluorescence. The *base*, liberated with N-sodium hydroxide and recrystallised from 60 parts of 60% alcohol, formed orange-yellow crystals, m. p. 271° (281°, corr.), slightly soluble in chloroform, ether, and acetone, very soluble in alcohol with a green fluorescence (Found: N, 11·0. $C_{14}H_{11}ON_2Cl$ requires N, 10·8%).

*5-Butylaminoacridine hydrochloride.* *n*-Butylamine (3·6 g., b. p. 76—78°), 5-chloroacridine (5 g.), and phenol (15 g.) were heated under reflux, the bath being raised from 70° to 130° during an hour. *5-Butylaminoacridine hydrochloride* was precipitated from the cooled mass with ether (50 ml.). It recrystallised from alcohol (9 ml.) in yellow needles (60% yield), m. p. 189—190°, and was soluble in 5 parts of boiling water and 1·5 parts of boiling alcohol. In ultra-violet light (λ 3650—3663 A.), but not in daylight, the aqueous solution fluoresces green, changing to an intense blue on dilution. The salt is very slightly soluble in acetone, benzene, and ether (Found: C, 71·1; H, 6·8; N, 9·6. $C_{17}H_{18}N_2$,HCl requires C, 71·2; H, 6·7; N, 9·75%). The base, recrystallised from benzene–light petroleum (3 : 1), formed orange-yellow crystals, m. p. 100—102°, very soluble in alcohol with a green fluorescence.

*cyclo*Hexylamine (3·1 g., b. p. 134—135°), 5-chloroacridine (5·35 g.), and phenol (15 g.) were heated at 120° for ½ hour, cooled, and the 5-cyclo*hexylaminoacridine hydrochloride* precipitated with ether (50 ml.) and recrystallised from alcohol (60 ml.); yield, 70% of greenish-yellow crystals, m. p. 271° (280° corr.; sealed tube), soluble in 11 parts of boiling alcohol and 16 parts of boiling water without marked fluorescence, and only slightly soluble in benzene or acetone (Found: C, 72·9; H, 7·0; N, 9·1. $C_{19}H_{20}N_2$,HCl requires C, 73·0; H, 6·8; N, 9·0%). The base, recrystallised from benzene, gave yellow crystals, m. p. 170—171°, very soluble in alcohol with a green fluorescence.

*5-Heptylaminoacridine hydrochloride*, similarly prepared in 70% yield from *n*-heptylamine (b. p. 154—156°) and recrystallised from water (300 ml.), gave yellow crystals, m. p. 106° (138° when anhydrous), soluble in its own weight of boiling alcohol and in 600 parts of cold water with very little fluorescence; moderately soluble in boiling benzene (Found: C, 69·6; H, 7·9. $C_{20}H_{24}N_2$,HCl,$H_2O$ requires C, 69·2; H, 7·8%).

Dodecylamine (2·4 g.; b. p. 133—135°/15 mm.), 5-chloroacridine (2·9 g.), and phenol (9 g.) were heated for ½ hour at 160°, and the phenol distilled off in a vacuum. The residue was stirred with light petroleum (30 ml.) and ether (90 ml.), kept on ice overnight, and the *5-dodecylaminoacridine hydrochloride* filtered off, washed with a little acetone, and recrystallised from acetone (130 ml.). Yield, 85% of yellow, slippery crystals, m. p. 92°, sparingly soluble in cold water with a brilliant blue fluorescence visible only in ultra-violet light. Soluble in its own weight of boiling benzene or of alcohol; soluble in about 700 parts of 30% alcohol (Found: C, 72·2; H, 9·0; N, 6·8. $C_{25}H_{34}N_2$,HCl,$H_2O$ requires C, 72·0; H, 9·0; N, 6·7%). The base, m. p. 67°, liberated from the alcoholic solution with N-sodium hydroxide (aqueous) and recrystallised from light petroleum, was yellow and more soluble in 10% acetic acid than in mineral acids. The alcoholic solution had a green fluorescence.

*5-Hexadecylaminoacridine hydrochloride*, similarly prepared (75% yield) from cetylamine (m. p. 44°), formed yellow, slippery needles, m. p. 99—100°, almost insoluble in boiling water, soluble in its own weight of boiling benzene and in about 200 parts of boiling acetone (Found: C, 73·3; H, 9·7; N, 6·0. $C_{29}H_{42}N_2$,HCl,$H_2O$ requires C, 73·6; H, 9·6; N, 5·9%). The base, crystallised from light petroleum and from 75% alcohol (green fluorescence), formed yellow crystals, m. p. 66°, readily soluble in a slight excess of 10% acetic acid.

We thank Messrs. F. H. Dorman and M. R. F. Mulcahy and Miss Beryl Reynolds for their experimental assistance in the surface-tension work.

UNIVERSITY OF SYDNEY, N.S.W. DEPARTMENT OF AGRICULTURE, AND UNIVERSITY OF MELBOURNE.

[*Received, October 23rd*, 1943.]

---

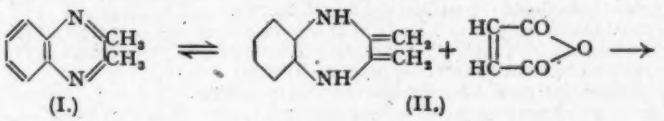
## 172. *The Diels–Alder Synthesis with 2 : 3-Dimethylquinoxaline. The Reaction between Maleic Anhydride and Anthranil.*

By A. SCHÖNBERG and AHMED MOSTAFA.

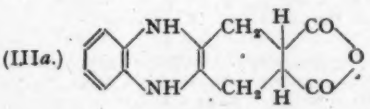
2 : 3-Dimethylquinoxaline, in the tautomeric form (II), reacts with maleic anhydride in the molecular proportion 1 : 1 and with *p*-benzoquinone in the proportion 2 : 1. Formulæ (III*a*) or (III*b*) and (IV*a*) or (IV*b*) respectively are advanced for the *products*. No reaction of this kind was observed between 2 : 3-dimethylquinoxaline and succinic anhydride or between maleic anhydride or *p*-benzoquinone and quinoxaline or its derivatives not capable of forming a diene system corresponding to (II). Anthranil reacts with maleic anhydride, forming a colourless *product* (VI*a* or VI*b*).

(I) 2 : 3-DIMETHYLQUINOXALINE (I), reacting in the tautomeric form (II) (Ogg and Bergstrom, *J. Amer. Chem. Soc.*, 1931, **53**, 1846), gives *addition products* when heated with maleic anhydride or with *p*-benzoquinone in toluene, by addition in the molecular proportion 1 : 1 in the former case and 2 : 1 in the latter. Both products can be sublimed in a vacuum and do not react with diazomethane and formulæ (III*a*) or (III*b*) and (IV*a*) or (IV*b*) respectively are proposed for them. The addition product (III*a*) or (III*b*) is soluble in alkali and is precipitated unchanged on careful neutralisation.

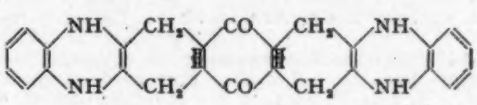
Further evidence that 2 : 3-dimethylquinoxaline can be applied in diene synthesis with maleic anhydride and *p*-benzoquinone was found in the fact that no reaction of this type occurred when quinoxaline, 2-methylquinoxaline, 2-phenyl-3-methylquinoxaline, and 2 : 3-diphenylquinoxaline were heated under the same conditions, or even more severe conditions, with maleic anhydride and with *p*-benzoquinone. The above-mentioned quinoxalines are not capable of forming a diene system. No reaction occurred when 2 : 3-dimethylquinoxaline was heated with succinic anhydride under similar conditions to those under which the reaction with maleic anhydride takes place, which shows that the double bond in maleic anhydride plays a part.



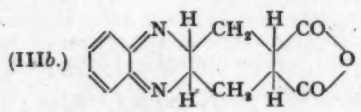
(I.) (II.)



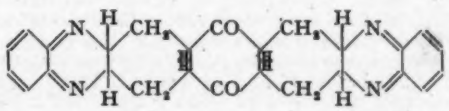
(III*a*.)



(IV*a*.)

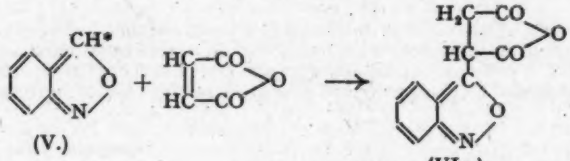


(III*b*.)

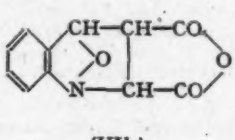


(IV*b*.)

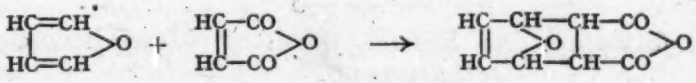
(II) A colourless *additive product* was obtained by reaction between maleic anhydride and anthranil (V) in molecular proportion. It sublimed without decomposition in a vacuum, decomposed when heated in air, yielding maleic anhydride and a red residue (a similar red residue is formed when anthranil is heated alone), was stable towards diazomethane, and dissolved in alkali and was precipitated unchanged on careful neutralisation. These properties do not allow us to state the structure of the addition product beyond doubt; we confine ourselves to the statement that, *inter alia*, formulæ (VI*a*) and (VI*b*) would explain the properties of the compound. Succinic anhydride did not react with anthranil to form an addition product under similar or even more severe conditions, possibly because it does not contain the necessary double bond. *C*-Phenylanthranil did not react with maleic anhydride, which may be explained by the fact that the hydrogen atom marked with an asterisk in (V) is essential for reaction (compare VI*a*); but the lack of reaction in this case may be due to steric hindrance. If (VI*b*) is the correct formula, the reaction is analogous to the action of maleic anhydride on furan (Diels and Alder, *Ber.*, 1929, **62**, 554); (VII), like the addition product of anthranil and maleic anhydride, decomposes on heating with the formation of maleic anhydride.



(V.) (VI*a*.)



(VI*b*.)



(VII.)

## Experimental.

*Maleic Anhydride and 2 : 3-Dimethylquinoxaline.*—2 : 3-Dimethylquinoxaline free from water of crystallisation (Gabriel and Sonn, *Ber.*, 1907, **40**, 4833) (0·5 g.; 1 mol.) and maleic anhydride (1 mol.) were refluxed in dry toluene (20 c.c.) for 2½ hours, a brown sticky substance separating. The mixture was left overnight in the refrigerator, the toluene then decanted, and the sticky material dissolved in hot glacial acetic acid and kept in the refrigerator; yellowish (slightly green) crystals (III*a* or III*b*) were obtained from the mother-liquor (A). The *addition product* was readily soluble in tetralin and methyl alcohol, with difficulty in chloroform and acetone; the sample for analysis was crystallised several times from glacial acetic acid; m. p. above 305°, but darkening was observed at that temperature (Found : C, 65·8; H, 4·8; N, 10·6. $C_{14}H_{12}O_3N_2$ requires C, 65·5; H, 4·7; N, 10·8%). On further refluxing for 3 hours, the mother-liquor (A) deposited more of the brown substance (total yield, about 0·4 g.).

The addition product (0·5 g.) was heated under reduced pressure in a bath at 260° for 15 minutes. After 5 minutes a brown sublimate formed; it was crystallised from acetic acid and proved to be the addition product.

A solution of the addition product in aqueous sodium hydroxide (30%) was cooled and treated dropwise with concentrated hydrochloric acid. The precipitate formed (it was soluble in excess of hydrochloric acid) was collected, washed, and crystallised from glacial acetic acid, and proved to be the initial material.

Even after refluxing for 1 hour with 10% sodium hydroxide solution the addition product was recovered unchanged.

*Succinic Anhydride and 2 : 3-Dimethylquinoxaline.*—Equimolecular amounts of 2 : 3-dimethylquinoxaline (0·5 g.) and succinic anhydride were refluxed in dry toluene (20 c.c.) for 6 hours, and the mixture kept for one night in a cooling mixture; succinic anhydride separated. From the mother-liquor, after concentration, 2 : 3-dimethylquinoxaline was obtained.

*Maleic Anhydride and Quinoxaline.*—Solutions of quinoxaline (Chattaway and Humphrey, J., 1929, 645) (1 g.; 1 mol.)

and maleic anhydride (1 mol.), each in hot dry toluene (15 c.c.), were mixed, refluxed for 3 hours, and then kept overnight in the refrigerator; no crystals separated and on concentration the initial materials were recovered. The same result was obtained after refluxing in dry xylene for 6 hours.

*Maleic Anhydride and 2-Methylquinoxaline.*—2-Methylquinoxaline (Bennett and Willis, J., 1928, 1960) (free from *o*-phenylenediamine; see below) and maleic anhydride in molecular proportion were dissolved in toluene (dried over sodium) and refluxed for 6 hours without formation of a deposit. The presence of unchanged 2-methylquinoxaline was shown by treating a portion of the product with *p*-nitrobenzaldehyde; the 2-*p*-nitrostyrylquinoxaline obtained did not depress the m. p. of an authentic specimen (Bennett and Willis, *loc. cit.*). Another portion, after removal of the toluene in a vacuum, left a brown liquid, from which a solid separated on cooling. This was washed with and crystallised from light petroleum, giving maleic anhydride (identified by mixed m. p.).

*Maleic Anhydride and 2-Phenyl-3-methyl- or 2 : 3-Diphenyl-quinoxaline.*—The quinoxaline (1 g.) and maleic anhydride (1 mol.) were refluxed in dry toluene (20 c.c.) for 3 hours, and the solution kept overnight in the refrigerator. No crystals separated and on concentration the initial materials were recovered.

The same results were obtained after 6 hours' refluxing in dry xylene.

*Maleic Anhydride and o-Phenylenediamine.*—To *o*-phenylenediamine (1 g.; 1 mol.) in toluene (10 c.c., dried over sodium) was added a hot solution of maleic anhydride (1 mol. in 10 c.c. of dry toluene); rapid precipitation of a yellow substance took place and the mixture was left in the refrigerator to complete the reaction. The *product* $C_6H_4(NH\cdot CO\cdot CH{:}CH\cdot CO_2H)_2$ was collected and washed with dry toluene; it separated from methyl alcohol in colourless crystals, m. p. 189—190°, readily soluble in alkali, methyl alcohol, ethyl alcohol and acetone (Found: C, 55·4; H, 4·1; N, 9·2. $C_{14}H_{12}O_6N_2$ requires C, 55·3; H, 3·9; N, 9·2%). The same product was obtained when 2 mols. of maleic anhydride were used.

p-*Benzoquinone and 2 : 3-Dimethylquinoxaline.*—A solution of equimolecular amounts of 2 : 3-dimethylquinoxaline (1 g.) and *p*-benzoquinone in dry toluene (20 c.c.) became brown after refluxing for 2½ hours. It was left overnight in the refrigerator and the crystalline *addition product* (IV*a* or IV*b*) (about 0·6 g.) was then collected and recrystallised from toluene, forming colourless needles, m. p. 190° (brown melt after shrinking at 189°), soluble in ether and benzene (Found: C, 73·5; H, 5·9; N, 12·6. $C_{28}H_{24}O_2N_2$ requires C, 73·5; H, 5·6; N, 13·2%).

The same substance was obtained when 2 mols. of 2 : 3-dimethylquinoxaline were treated with 1 mol. of *p*-benzoquinone under similar conditions.

The addition product was heated (boiling nitrobenzene bath) in a sublimation apparatus through which carbon dioxide was passed. After 15 minutes a colourless sublimate of needles formed, m. p. 190°, not depressed by the original addition product.

p-*Benzoquinone and Quinoxaline.*—A solution of equimolecular amounts of quinoxaline (1 g.) and *p*-benzoquinone in dry benzene (20 c.c., thiophen-free) was heated in a sealed tube at 110° for 3 hours; the benzene was then evaporated in a vacuum, and the residue divided into two portions. One portion was extracted with water; from the aqueous solution ether extracted quinoxaline (0·8 g.). From the other portion, on concentration, *p*-benzoquinone was obtained.

p-*Benzoquinone and 2 : 3-Diphenylquinoxaline.*—The two substances were recovered unchanged after a solution of equimolecular amounts of 2 : 3-diphenylquinoxaline (Hinsberg and König, *Ber.*, 1894, **27**, 2181) (1 g.) and *p*-benzoquinone in dry xylene (20 c.c.) had been refluxed for 3 hours, concentrated, and cooled.

*Anthranil and Maleic Anhydride.*—Equimolecular amounts of anthranil (1 g.) and maleic anhydride in dry toluene (20 c.c.) were heated on a water-bath for ½ hour, and the mixture left for 1 day in the refrigerator. The *addition product* obtained separated from chloroform in fine colourless or almost colourless crystals, m. p. about 150° (some decomp.) (Found: C, 60·5; H, 3·1; N, 6·6. $C_{11}H_7O_4N$ requires C, 60·8; H, 3·2; N, 6·4%), readily soluble in benzene, carbon tetrachloride, and methyl alcohol. It dissolved in aqueous sodium hydroxide and was reprecipitated by concentrated hydrochloric acid. It sublimed when heated in a vacuum (bath temperature about 60°). When heated in a sublimation apparatus, at first without vacuum, it became red and melted; then, under vacuum, at a bath temperature of 210°, maleic anhydride condensed on the walls.

*Succinic Anhydride and Anthranil.*—Equimolecular amounts of anthranil (1 g.) and succinic anhydride were refluxed in toluene (20 c.c., dried over sodium) for 3 hours or in phenetole for 6 hours, but were recovered unchanged.

*Maleic Anhydride and C-Phenylanthranil.*—*C*-Phenylanthranil (Bamberger and Lindberg, *Ber.*, 1909, **42**, 1723) (1 g.) was recovered unchanged after being subjected to the procedure described in the case of anthranil and maleic anhydride.

FOUAD I UNIVERSITY, CAIRO, EGYPT. [*Received, June 11th*, 1943.]

## 173. *The Complex-formation and Rearrangement of* p-*Hydroxylaminobenzenesulphonamide.*

By H. BURTON and N. WALKER.

Confirmatory evidence has been obtained to show that *p*-hydroxylaminobenzenesulphonamide and sulphanilamide form a complex, m. p. 161°. The rearrangement of *p*-hydroxylaminobenzenesulphonamide in dilute acid solution to *p*-aminophenol and azoxybenzene-4 : 4′-disulphonamide has been carried out.

THE recent work of Sevag (*J. Amer. Chem. Soc.*, 1943, **65**, 110) has considerably clarified the confusion which had arisen regarding the identity of *p*-hydroxylaminobenzenesulphonamide, of which two crystalline forms with different m. p.'s had been reported by various workers (Mayer, *Biol. méd. suppl.*, 1937, **27**, 45; Bratton, White, and Marshall, *Proc. Soc. Exp. Biol. Med.*, 1939, **42**, 847; Burton, *Chem. and Ind.*, 1941, **60**, 449; Sevag and Shelburne, *J. Bact.*, 1942, **43**, 421). On the grounds of differences in solubilities and salt-forming properties, elementary analysis, oxygen consumption, and the colorimetric estimation of sulphanilamide by Ehrlich's reagent after removal of hydroxylamine by oxidation, Sevag concludes that the form with m. p. 161·5° is a complex of two molecules of *p*-hydroxylaminobenzenesulphonamide with one molecule of sulphanilamide, and that the form, m. p. 140°, is pure *p*-hydroxylaminobenzenesulphonamide. We have obtained additional evidence which supports this constitution for the higher-melting form, namely, the isolation of sulphanilamide after removal of *p*-hydroxylaminobenzenesulphonamide by air oxidation, the isolation of *N*-acetyl-*p*-hydroxylaminobenzenesulphonamide and of $N^4$-acetylsulphanilamide from the product obtained by acetylating the

higher-melting form, and by the synthesis of the higher-melting complex by crystallisation of a mixture of one molecule of sulphanilamide with two molecules of *p*-hydroxylaminobenzenesulphonamide from warm water.

Since Mayer (*loc. cit*) put forward the view that the bacteriostatic action of sulphanilamide is due to its oxidation to *p*-hydroxylaminobenzenesulphonamide various workers have investigated possible oxidation products of sulphanilamide. Thorpe, Williams, and Shelswell (*Biochem. J.*, 1941, **35**, 52) reject James' claim (*ibid.*, 1940, **34**, 640) to have isolated *p*-hydroxylaminobenzenesulphonic acid and acetyl-*p*-hydroxylaminobenzenesulphonamide from urine and suggest that the most likely oxidation products of sulphanilamide to be produced *in vivo* are 4-amino-3-hydroxybenzenesulphonamide and 4-amino-2-hydroxybenzenesulphonamide; further, they state: "If the formation of an *o*- or *m*-aminophenolsulphonamide could be proved it would argue against the correctness of the hydroxylamino hypothesis, in that there is no example in the literature of the transformation of a hydroxylamine into an *o*- or *m*-aminophenol." The latter statement is only partially correct (see Bamberger and Laguth, *Ber.*, 1898, **31**, 1500; Bamberger, *Ber.*, 1900, **33**, 3600). Thorpe *et al.* (*loc. cit.*) also found that if urines, from rabbits which had been relatively highly dosed with sulphanilamide, were boiled with dilute hydrochloric acid for a few minutes, a diazo-reaction after acetylation was no longer given (a solution of *p*-hydroxylaminobenzenesulphonamide still gave the acetylated diazo-reaction after boiling with hydrochloric acid under similar conditions) and attribute this result to an *o*-aminophenol derivative, *e.g.*, 4-amino-3-hydroxybenzenesulphonamide. We have found, however, that *p*-hydroxylaminobenzenesulphonamide, on heating with dilute sulphuric or hydrochloric acid in an atmosphere of carbon dioxide on the water-bath, is converted into azoxybenzene-4 : 4'-disulphonamide and *p*-aminophenol. Thus, the above argument used by Thorpe *et al.* (*loc. cit.*) against the correctness of the hydroxylamine hypothesis of sulphanilamide oxidation is shown not to be a valid one and this possibility must be considered as still open. This result also amplifies the statement of Bratton *et al.* (*loc. cit.*) that in acid solution *p*-hydroxylaminobenzenesulphonamide is fairly stable and apparently goes only into the azoxy-compound; in neutral or alkaline solution decomposition is accelerated and both the azoxy-compound and sulphanilamide are formed. No *p*-aminophenol was detected by the indophenol test by the present authors when the higher-melting complex in faintly alkaline solution was oxidised by air at room temperature.

## Experimental.

Microanalyses were carried out by Dr. G. Weiler and Dr. F. B. Strauss of Oxford.

The "complex," m. p. 161·5°, of *p*-hydroxylaminobenzenesulphonamide and sulphanilamide was prepared by Burton's method (*loc. cit.*). *p*-Hydroxylaminobenzenesulphonamide prepared as described by Bratton, White, and Marshall had m. p. 140°, unchanged on recrystallisation from air-free water (Found: C, 38·4; H, 4·5; N, 14·4, 14·8. Calc. for $C_6H_8O_3N_2S$: C, 38·3; H, 4·25; N, 14·9%). We found, however, that the first-named method sometimes gave the hydroxylamine, m. p. 140°, and that the second method occasionally afforded the "complex."

*Acetylation of the "Complex."*—The "complex" (1·77 g.) and acetic anhydride (1·1 g.), stirred at room temperature, set to a hard white mass. The product was dissolved in hot methyl alcohol (25 ml.); the filtered solution, on cooling, deposited crystalline *N*-acetyl-*p*-hydroxylaminobenzenesulphonamide (0·51 g.), m. p. 220° (decomp.). After recrystallisation from aqueous alcohol it formed small colourless plates, m. p. 224° (decomp.), (Found: C, 41·8; H, 4·4; N, 12·25; S, 14·3. Calc. for $C_8H_{10}O_4N_2S$: C, 41·7; H, 4·35; N, 12·2; S, 13·9%). It gave an intense blood-red colour with dilute ferric chloride solution, as stated by Bratton *et al.* (*loc. cit.*). The methyl-alcoholic filtrate, evaporated to dryness, left a solid (1·45 g.), m. p. 140—160°, which was fractionally crystallised twice from methyl alcohol and finally fractionated from water; after filtration of a little *N*-acetyl-*p*-hydroxylaminobenzenesulphonamide, long colourless needles of $N^4$-acetylsulphanilamide (4—5 mg.), m. p. 216—217°, not depressed by an authentic specimen, were obtained.

*Oxidation of the "Complex" by Air.*—The "complex" (0·5 g.) was dissolved in water (25 ml.), 3 drops of concentrated aqueous ammonia added, and air aspirated through the solution for 3 hours at room temperature. Azoxybenzene-4 : 4'-disulphonamide (0·238 g.) was removed and the filtrate, which gave no reaction with cold, ammoniacal silver nitrate and did not show an indophenol reaction, was evaporated to dryness, yielding a residue (0·215 g.), m. p. 155—158°. After twice recrystallising from water, sulphanilamide, m. p. 163—164°, not depressed by an authentic specimen, was obtained.

*Synthesis of the "Complex."*—*p*-Hydroxylaminobenzenesulphonamide (0·056 g.), m. p. 141—142°, and sulphanilamide (0·025 g.) were placed in the hollow stopper of a Thunberg tube, water (3 ml.) was put in the tube, and it was then evacuated and closed. On warming and mixing the contents of the tube, a clear solution was obtained. When this was cooled in ice, colourless crystals of the "complex" separated, m. p. 161—162°, depressed by sulphanilamide but not by the complex prepared by Burton's method.

*Rearrangement of the "Complex."*—A solution of the "complex" (3 g.) in air-free water (80 ml.) and concentrated sulphuric acid (4 g.) through which carbon dioxide was slowly passing was heated on the steam-bath for 6 hours. The mixture was cooled, and azoxybenzene-4 : 4'-disulphonamide (0·7 g.), m. p. 295° (decomp.), removed. The cold filtrate was made neutral to Congo-red paper with solid sodium hydrogen carbonate; after a few minutes, nearly pure sulphanilamide (0·47 g.) separated, m. p. 158—160°, and, after recrystallisation from water, m. p. 164°, not depressed by an authentic specimen. The filtrate from the sulphanilamide, on treatment with potassium hydroxide (3 g.) and benzoyl chloride (3 ml.), gave a solid, which was collected, washed with water, and crystallised from alcohol, giving nearly colourless, small plates of *ON*-dibenzoyl-*p*-aminophenol (0·11 g.), m. p. 230—231°, raised to 232° by recrystallisation from methyl alcohol and not depressed by an authentic specimen. The rearrangement was also carried out with 5% hydrochloric acid in place of sulphuric acid and the same products were obtained.

*Rearrangement of* p-*Hydroxylaminobenzenesulphonamide.*—This (0·5 g.), m. p. 140°, in air-free water (20 ml.) and concentrated sulphuric acid (1 g.) was treated as was the complex in the preceding experiment. The filtrate from the azoxybenzene-4 : 4'-disulphonamide (0·185 g.), m. p. 300° (decomp.), was neutralised with solid sodium hydrogen carbonate and cooled in ice. Nothing separated, but on shaking with sodium hydroxide (2 g.) and benzoyl chloride (2 g.) *ON*-dibenzoyl-*p*-aminophenol (0·072 g.) was obtained; after crystallisation from absolute alcohol it had m. p. 230—231°, not depressed by an authentic specimen.

We thank I.C.I. (Dyestuffs), Ltd., and Messrs. Newton Chambers and Co., Ltd., for maintenance grants to one of us (N. W.), and Professor J. W. McLeod, F.R.S., for his interest in this investigation.

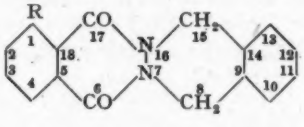
The University, Leeds, 2. [*Received, August 3rd*, 1943.]

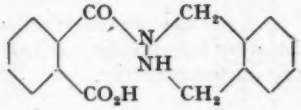
# 174. *Heterocyclic Nitrogen Compounds. Part I. Derivatives of 7 : 16-Diazanaphthacene.*

By H. H. Hatt and (Miss) E. F. M. Stephenson.

The synthesis of 6 : 17-*diketo*-6 : 8 : 15 : 17-*tetrahydro*-7 : 16-*diazanaphthacene* (I, R = H) has been achieved by condensation of (1) *o*-xylylene dibromide with phthalaz-1 : 4-dione and (2) phthaloyl chloride with 1 : 2 : 3 : 4-tetrahydrophthalazine hydrochloride. The second method has been used to obtain the 1-*nitro*- and the 1-*amino*-derivative.

The study of compounds derived from 7 : 16-diazanaphthacene was commenced because they belong to a class of compound which offered a new method of approach for the resolution of compounds owing their asymmetry to the disposal of valencies around tervalent nitrogen atoms. In these compounds two ring systems are fused together through vicinal nitrogen atoms and the non-planar disposal of the nitrogen valencies would require that the portions of the molecule on either side of the 7 : 16 nitrogen–nitrogen bond lie in different planes. Suitable substitution at a carbon atom of a benzenoid nucleus would then give an asymmetric molecule. For racemisation to occur, it would be necessary for both nitrogen atoms to pass through the planar condition, which might be expected to require a higher energy of activation than for a like change with a single tervalent nitrogen atom linked to three independent radicals. One of the probable causes of the failure to resolve tervalent nitrogen compounds should thus be either reduced or eliminated (compare Maitland, *Ann. Reports*, 1939, 241). The present work describes the preparation of some diketo-compounds of this class. It is proposed later to investigate the stereochemical properties of compounds of this class and especially of the reduced tetrahydrodiazanaphthacenes suitably substituted in one of the benzene nuclei.

(I.) 

 (II.)

6 : 8 : 15 : 17-Tetraketo-6 : 8 : 15 : 17-tetrahydro-7 : 16-diazanaphthacene was described by Drew and Hatt (J., 1937, 16). The preparation of substituted compounds of that type was found by them to be difficult and for this reason we have investigated direct syntheses of more reduced compounds rather than attempting the reduction of their tetraketo-compounds.

The *diketo*-compound (I, R = H) was obtained in 65% yield by heating together *o*-xylylene dibromide and phthalaz-1 : 4-dione; from the considerable amount of tarry matter also formed, only *N*-phthalimidophthalimide could be isolated. 5-Nitrophthalaz-1 : 4-dione and 6-chlorophthalaz-1 : 4-dione reacted with xylylene dibromide, but gave intractable resins, showing that this method of synthesis is of limited application.

That a phthalazine ring was formed in this reaction with *o*-xylylene dibromide was shown by ring cleavage with alcoholic sodium ethoxide to 2-*o*-carboxybenzoyltetrahydrophthalazine (II), which was subsequently oxidised to phthalic acid and phthalazine.

The second method of preparation of (I, R = H) by condensation of phthaloyl chloride and tetrahydrophthalazine hydrochloride proceeded smoothly and appears to be a general method.

## Experimental.

All m. p.'s are corrected.

6 : 17-*Diketo*-6 : 8 : 15 : 17-*tetrahydro*-7 : 16-*diazanaphthacene* (I, R = H).—(1) A mixture of dry phthalaz-1 : 4-dione (16·2 g.) and *o*-xylylene dibromide (27·5 g.) was heated under reflux at 215—220° with exclusion of moisture and occasional shaking. After ½ hour the product was allowed to cool and ground with alcohol. The crystalline powder was collected, washed with alcohol to remove tar-like impurities, and refluxed with glacial acetic acid (50 ml.) and hydrazine hydrate (1·3 ml.) for 2 hours to destroy the *N*-phthalimidophthalimide present. The product was poured into water, and the solid collected, washed, ground with 2N-ammonia, left overnight, and washed with water (acidification of the filtrates precipitated phthalaz-1 : 4-dione). The dry crude product (17—18 g.) crystallised from alcohol (charcoal) in faintly yellowish leaflets, m.p. 196·5—197·5°, easily soluble in chloroform or acetic acid and soluble in about 12 parts of boiling benzene or 30 parts of hot alcohol [Found: C, 72·4; H, 4·5; N, 10·7; *M* (in camphor), 266. $C_{16}H_{12}O_2N_2$ requires C, 72·7; H, 4·5; N, 10·6%; *M*, 264].

Attempts to carry out the condensation in nitrobenzene, tetralin or quinoline were unsuccessful.

(2) 1 : 2 : 3 : 4-Tetrahydrophthalazine hydrochloride (0·09 g.), phthaloyl chloride (0·15 ml.), and a few ml. of dry pyridine were refluxed for 3 hours with exclusion of moisture. After standing, water was added, the mixture evaporated to dryness on a water-bath, the brown crystalline residue made alkaline with N-sodium hydroxide, and the crystalline material collected and washed. Yield 0·12 g., m. p. 191—193° and, after one crystallisation from alcohol, 195—197°, not depressed by the material prepared by method (1).

The *diketo*-compound (I, R = H) gave a colourless solution in sulphuric acid, from which it was recovered unchanged by addition of water. The colourless solution slowly developed a permanent bright green colour at 170—190°. Dilute aqueous acids, hydriodic–acetic acid mixtures (1 : 1), and alcoholic hydrazine were without action on (I, R = H). Hot dilute aqueous alkali slowly dissolved it.

2-*o*-*Carboxybenzoyl*-1 : 2 : 3 : 4-*tetrahydrophthalazine* (II).—The diketo-compound (I, R = H) (0·5 g.) and 4N-alcoholic sodium ethoxide (16 ml.) were warmed on a water-bath, and the precipitated *sodium* salt of (II) collected, washed with absolute alcohol and ether, and dried under reduced pressure (yield, 0·52 g.) (Found: Na, 7·5. $C_{16}H_{13}O_3N_2Na$ requires Na, 7·55%). This salt was unchanged by prolonged refluxing with alcoholic sodium ethoxide.

The *acid* was precipitated on mixing an ice-cold solution of the sodium salt in 30 parts of water with a little more than the theoretical quantity of 0·5N-hydrochloric acid; it contained water of crystallisation. Cyclisation of the acid to (I, R = H) proceeded slowly at room temperature and rapidly at 70° (Found: equiv., 321; loss by cyclisation at 80° under reduced pressure, 18·9, 19·2, 19·0. $C_{16}H_{14}O_3N_2,2\frac{1}{2}H_2O$ requires equiv., 325; loss, 19·3%).

*Oxidation of the Sodium Salt.*—The salt (0·166 g.) in 0·2N-sodium hydroxide (30 ml.) was cooled to 2°, and 1% potassium permanganate solution (115 ml.) stirred in during 1 hour. After 6 hours the manganese dioxide was removed and washed and the combined liquids were made strongly alkaline and repeatedly extracted with chloroform. The extracts yielded 0·64 g. of phthalazine, m. p. 90—91° after crystallisation from chloroform and ether; it was identified by mixed m. p. and by conversion into the methiodide. Acidification and ether extraction of the alkaline liquor yielded 0·5 g. of phthalic acid containing traces of a nitrogen-containing acid from which it could be freed by sublimation.

1-*Nitro*-6 : 17-*diketo*-6 : 8 : 15 : 17-*tetrahydro*-7 : 16-*diazanaphthacene* (I, R = $NO_2$).—Tetrahydrophthalazine hydrochloride (3·1 g.), 3-nitrophthaloyl chloride (6 g.), and dry pyridine (12 ml.) were mixed, and the reddish-brown product heated to refluxing for 3 hours. The excess of pyridine was removed by heating under reduced pressure, and the residue made alkaline with aqueous sodium carbonate. The brown oil which first separated quickly solidified. Considerable losses occurred during purification from tar and a crystalline by-product. The *product*, washed with dilute mineral acid and water and repeatedly crystallised from chloroform–alcohol (charcoal), formed yellow parallelepipeds, m. p. 249—250° (slight decomp.) (Found: C, 62·4; H, 4·0; N, 13·7. $C_{16}H_{11}O_4N_3$ requires C, 62·1; H, 3·6; N, 13·6%). It dissolved readily in chloroform and acetic acid, sparingly in alcohol and acetone, and very sparingly in ether. Its constitution was confirmed by conversion into the red sodium salt of the acid analogue of (II), followed by oxidation with potassium permanganate in a similar manner to that described for (II) to give phthalazine and 3-nitrophthalic acid.

1-*Amino*-6 : 17-*diketo*-6 : 8 : 15 : 17-*tetrahydro*-7 : 16-*diazanaphthacene* (I, R = $NH_2$).—Stannous chloride (4·5 g.) in concentrated hydrochloric acid (21 ml.) was added to a stirred suspension of the nitro-compound (2·25 g.) in water maintained at 50—70°. After 7—8 hours the mixture was made strongly alkaline with sodium hydroxide and, after standing, filtered, and the *amine* extracted from the precipitate with alcohol. It separated from alcohol in pale yellow rhombs, m. p. 185—187° (decomp.) depending on the rate of heating [Found: C, 68·1; H, 4·7; N, 15·1, 15·2; *M* (in camphor), 268. $C_{16}H_{13}O_2N_3$ requires C, 68·8; H, 4·7; N, 15·0%; *M*, 279]. Alcoholic hydrazine hydrate reduced the nitro-compound to an impure amine.

The *benzoyl* derivative of (I, R = $NH_2$), obtained by the Schotten–Baumann method, crystallised from trichloroethylene and alcohol in fine white needles, m. p. 260—261° (slight decomp.) (Found: N, 10·9. $C_{23}H_{17}O_3N_3$ requires N, 11·0%). The amine can be diazotised by Schoutissen's method (*J. Amer. Chem. Soc.*, 1933, **55**, 4531) and the diazotised solution couples normally with β-naphthol.

1 : 2 : 3 : 4-*Tetrahydrophthalazine Hydrochloride*.—The phthalazine for this preparation was obtained from ωωω'ω'-tetrachloro-*o*-xylene, the method of Gabriel and Pinkus (*Ber.*, 1893, **26**, 2210) being followed except that, in agreement with Paul (*Ber.*, 1899, **32**, 2015), the use of chloroform rather than of benzene was found necessary for complete extraction.

Preparation of tetrahydrophthalazine hydrochloride by the method of Gabriel and Pinkus (*loc. cit.*) gave poor yields due to the method of isolation. Yields, 90% of the theoretical, were obtained as follows: The phthalazine hydrochloride was reduced with a 7% sodium amalgam at 20—25° and, after an unidentified product (yellow crystals, m. p. 229—231°, from alcohol) had been removed, the alkaline filtrate was extracted repeatedly with chloroform. The tetrahydrophthalazine hydrochloride was then precipitated from the dried chloroform solution by saturation with dry hydrogen chloride. The product was sufficiently pure for preparative purposes.

6-*Chlorophthalaz*-1 : 4-*dione*.—4-Chlorophthalimide (Levy and Stephens, J., 1931, 79) (4·54 g.), 100% hydrazine hydrate (6 ml.), and alcohol (50 ml.) were refluxed on a water-bath for 2 hours, and the bulk of the alcohol removed. The residue was dissolved in 5% aqueous sodium hydroxide (charcoal), and the *dione* precipitated from the filtrate with hydrochloric acid. The precipitated material was almost pure, but could be crystallised from acetic acid or sublimed. It formed fine white needles, m. p. 348—350° (in a sealed tube) (Found: C, 49·2; H, 2·6; N, 14·3. $C_8H_5O_2N_2Cl$ requires C, 48·9; H, 2·6; N, 14·3%).

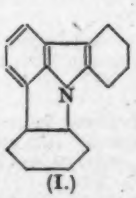
THE UNIVERSITY OF MELBOURNE. [*Received, May 24th*, 1943.]

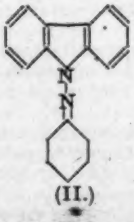
## 175. *Attempts to prepare Optically Active Tervalent Nitrogen Compounds. Part II.* 1 : 9-(2' : 3' : 4' : 5'-*Tetrahydrophenylene*)*carbazole*.

By ROBERT W. G. PRESTON and S. HORWOOD TUCKER.

Diphenylenehydrazones of *cyclo*hexanone, acetone, pyruvic acid, methyl pyruvate, ethyl acetoacetate, and ethyl oxaloacetate have been prepared. The first has been indolised to *tetrahydrophenylenecarbazole*, which has been dehydrogenated to 1 : 9-phenylenecarbazole. This has also been synthesised from 1-nitrocarbazole, thus corroborating its synthesis from carbazole.

MANJUNATH (*J. Indian Chem. Soc.*, 1927, **4**, 271), by reduction of 9-nitrosohexahydrocarbazole with zinc and acetic acid in presence of *cyclo*hexanone, the solution then being heated, prepared a substance, $C_{18}H_{21}N$, to which he gave an obviously incorrect structural formula. This was rectified by Lions and Ritchie (*J. Roy. Soc. N.S.W.*, 1939, **73**, 127), and the compound correctly represented by (I)—" 8 : 9-(1 : 2-*cyclo*hexylene)tetrahydrocarbazole."


(I.)


(II.)

(III.)

Manjunath (*loc. cit.*, p. 280) also prepared *cyclo*hexanone diphenylenehydrazone (II), but failed to indolise it into 1 : 9-(2' : 3' : 4' : 5'-*tetrahydrophenylene*)*carbazole* (III). We have been able to effect this indolisation

(yield, 21%) by heating the hydrazone (II) with dry hydrogen chloride in tetralin maintained at 160° for ¾ hour (cf. Robinson and Robinson, J., 1918, **113**, 639, 644; Perkin and Plant, J., 1924, **125**, 1503, 1509). The tetrahydrophenylenecarbazole (III) was readily dehydrogenated to 1:9-phenylenecarbazole (Dunlop and Tucker, J., 1939, 1945) by heating with sulphur in quinoline. Manjunath failed to dehydrogenate " 8 : 9-(1 : 2-*cyclo*hexylene)tetrahydrocarbazole " (I) by heating with sulphur, but by means of heated lead monoxide a dehydrogenation product, m. p. 140°, was obtained in too small quantity for investigation. It may have been 1 : 9-phenylenecarbazole (m. p. 136·5—138·5°, corr.).

The above synthesis of 1 : 9-phenylenecarbazole supports the previous formulation : a conclusive synthesis has now been carried out by the reaction of 1-nitrocarbazole (Preston, Tucker, and Cameron, J., 1942, 500) and iodobenzene to give 1-*nitro*-9-*phenylcarbazole*, which by reduction to 1-*amino*-9-*phenylcarbazole*, followed by diazotisation in acetic–sulphuric acid solution, cyclised to give 1 : 9-phenylenecarbazole (see Dunlop and Tucker, *loc. cit.*).

Formerly we endeavoured to rigidify a non-planar configuration of the nitrogen bonds by having benzene rings fused to two pyrrole rings, as in 1 : 9-phenylenecarbazole (Dunlop and Tucker, *loc. cit.*) : we do not expect to be able to obtain compounds of the constrained type from reduced phenylenecarbazoles, since reduced rings are mobile, and accordingly will relieve strain instead of imposing it.

We have prepared *diphenylenehydrazones* of acetone, pyruvic acid, methyl pyruvate, ethyl acetoacetate and ethyl oxaloacetate. Attempts to indolise these have been discouraging but are to be continued.

## Experimental.

9-Aminocarbazole (Wieland, Süsser, and Fressel, *Annalen*, 1912, **392**, 183) forms colourless crystals, from carbon tetrachloride : it gives an orange-red *picrate*, m. p. 136—138° (Found : C, 52·9; H, 3·2; N, 16·8. $C_{12}H_{10}N_2,C_6H_3O_7N_3$ requires C, 52·6; H, 3·1; N, 17·0%).

cyclo*Hexanone Diphenylenehydrazone*.—A mixture of 9-aminocarbazole (4·55 g.) and *cyclo*hexanone (freshly distilled, 5 g.; 2 mols.) was gently warmed over a free flame until reaction set in. After the reaction had subsided, the mixture was boiled (½ min.), and the product dissolved in carbon tetrachloride; carbazole separated on cooling. The filtrate was evaporated, and the residue crystallised from ethanol. More carbazole at first separated (total yield, 0·85 g.; 20%), then the hydrazone, m. p. 96° (4·25 g.; yield, 65%). The hydrazone grew out of solution slowly and so facilitated the troublesome removal of carbazole.

When reaction was brought about by heating (2½ hours) in alcohol (Manjunath, *loc. cit.*, p. 280), the yields of hydrazone and of carbazole were both slightly lower.

Attempts to prepare the hydrazone from 9-nitrosocarbazole without isolation of 9-aminocarbazole (cf. Manjunath, *loc. cit.*, p. 280; Lions and Ritchie, *loc. cit.*, p. 136) gave greatly reduced yields (~25%).

1 : 9-(2′ : 3′ : 4′ : 5′-*Tetrahydrophenylene*)*carbazole*.—A solution of *cyclo*hexanone diphenylenehydrazone (2 g.) in tetralin (distilled over sodium; 20 ml.) was added in small amounts during 30 mins. to tetralin (10 ml.) heated in a metal bath (160°), dry hydrogen chloride being continuously bubbled through during this period and a subsequent 30 minutes' heating. After removal of a mustard-coloured precipitate (0·9 g.) the tetralin was removed in steam, and the pale yellow residue dissolved in boiling carbon tetrachloride. After cooling, carbazole (0·2 g.) was removed, the solution evaporated, and the residue crystallised from methanol–acetone (1 : 1) to give colourless needles of 1 : 9-(2′ : 3′ : 4′ : 5′-*tetrahydrophenylene*)*carbazole*, m. p. 99—100° (0·4 g.; yield, 21%) (Found : C, 88·0; H, 6·2; N, 5·7. $C_{18}H_{18}N$ requires C, 88·2; H, 6·1; N, 5·7%).

When the hydrazone (2 g.) was added all at once to the tetralin (25 ml.) through which hydrogen chloride was passing at 160°, and the mixture maintained at this temperature for ¾ hour, the yield was slightly less.

Addition of anhydrous zinc chloride (1 g.) was without appreciable effect.

Whenever reagents containing water were used (Hughes, Lions, and Ritchie, *J. Roy. Soc. N.S.W.*, 1938, **72**, 213) a high yield of carbazole was obtained; boiling the hydrazone in glacial acetic acid gave rise to 9-acetamidocarbazole, m. p. 247°.

The s-*trinitrobenzene* compound was prepared in and crystallised from ethanol, forming orange-red needles, m. p. 164—166° (Found : C, 62·8; H, 4·1; N, 12·3. $C_{18}H_{16}N,C_6H_3O_6N_3$ requires C, 62·9; H, 3·9; N, 12·2%).

The *picrate* was prepared in and crystallised from ethanol, forming bronze-coloured needles, m. p. 159—160° (Found : C, 60·6; H, 3·8; N, 12·0. $C_{18}H_{18}N,C_6H_3O_7N_3$ requires C, 60·8; H, 3·8; N, 11·8%).

1 : 9-*Phenylenecarbazole*.—Dehydrogenation of 1 : 9-(2′ : 3′ : 4′ : 5′-tetrahydrophenylene)carbazole (0·1 g.) was effected by boiling its solution in quinoline (2 ml.) containing sulphur (0·026 g.) for 2 hours. The mixture was treated with excess of dilute hydrochloric acid and extracted with ether; the residue obtained on evaporation of the ether sublimed at 260—270°/12 mm. The product crystallised from methanol–acetone (1 : 1) in colourless, silky needles having alone or admixed with 1 : 9-phenylenecarbazole (Dunlop and Tucker, *loc. cit.*) m. p. 136·5—138·5° (corr.). The identity was confirmed by means of the s-trinitrobenzene compound.

*Pyruvic Acid Diphenylenehydrazone*.—A solution of pyruvic acid (4·5 g.) and 9-aminocarbazole (4·5 g.) in ethanol (15 ml.) was boiled for 15 minutes. On cooling, the hydrazone separated in flat, yellow needles, m. p. 157—160° (decomp.) (5·35 g.; yield, 85%) (Found : C, 71·4; H, 4·8; N, 11·0. Calc. : C, 71·4; H, 4·8; N, 11·1%) [Barger and Dyer, *J. Amer. Chem. Soc.*, 1938, **60**, 2414, give m. p. 148—150° (decomp.)].

*Methyl pyruvate diphenylenehydrazone*, prepared by the action of diazomethane (ether) on the acid in the usual way, separated from methanol in stumpy, lemon-yellow crystals, m. p. 89—90° (Found : C, 72·2; H, 5·4; N, 10·4. $C_{16}H_{14}O_2N_2$ requires C, 72·2; H, 5·3; N, 10·5%).

*Ethyl acetoacetate diphenylenehydrazone*, prepared similarly to the pyruvic acid hydrazone above, or by heating 9-aminocarbazole in excess of ethyl acetoacetate on a boiling water-bath for 15 minutes, separated from methanol in colourless, craggy crystals, m. p. 113°, after softening at 108° (yield, nearly 100%) (Found : C, 73·7; H, 6·0; N, 9·7. $C_{18}H_{18}O_2N_2$ requires C, 73·5; H, 6·1; N, 9·5%).

*Ethyl oxaloacetate diphenylenehydrazone* was prepared, as for the acetoacetate hydrazone, in good yield from 9-aminocarbazole and ethyl oxaloacetate. It was obtained in pale green prisms from methanol and recrystallised from light petroleum (b. p. 60—80°); m. p. 85—87° (Found : C, 68·3; H, 5·8; N, 8·1. $C_{20}H_{20}O_4N_2$ requires C, 68·2; H, 5·7; N, 8·0%).

*Acetone diphenylenehydrazone*, obtained by boiling a solution of 9-aminocarbazole in excess of acetone for 1½—2 hours, crystallised from light petroleum (b. p. 40—60°) in colourless, fluffy balls of needles, m. p. 78—81° (yield, 85%) (Found : C, 80·9; H, 6·3; N, 12·7. $C_{15}H_{14}N_2$ requires C, 81·1; H, 6·3; N, 12·6%).

1-*Nitro*-9-*phenylcarbazole*.—A mixture of 1-nitrocarbazole (1·2 g.), iodobenzene (6 ml.), anhydrous potassium carbonate (1·2 g.), and copper bronze (0·01 g.) was boiled (metal bath) for 6 hours. More potassium carbonate (0·5 g.) was added (there was effervescence and the colour of the liquid changed from yellow to red) and heating was continued for 2 hours. The excess of iodobenzene was removed by distillation, and the residue treated with dilute hydrochloric acid, washed with water, and extracted with boiling light petroleum (b. p. 80—100°). From the filtered extract, nearly pure product separated on cooling. Recrystallisation from methanol or from benzene–light petroleum (b. p. 80—100°) gave stout yellow prisms of 1-*nitro*-9-*phenylcarbazole*, m. p. 130—132° (1·1—1·2 g.; yield, >70%) (Found: C, 75·0; H, 4·3; N, 9·9. $C_{18}H_{12}O_2N_2$ requires C, 75·0; H, 4·2; N, 9·7%).

1-*Amino*-9-*phenylcarbazole*.—A mixture of 1-nitro-9-phenylcarbazole (0·8 g.) and sodium sulphide ($Na_2S,9H_2O$, 2 g.) in ethanol (10 ml.) was boiled for 3 hours. Water was added to the boiling solution until turbidity was produced. The material which separated on cooling was extracted with boiling light petroleum (b. p. 60—80°) and crystallised from this solvent, then from ethanol (+ drop of water), giving pale brown laminæ of 1-*amino*-9-*phenylcarbazole*, m. p. 96—98° (0·33 g.; yield, 46%) (Found: C, 83·9; H, 5·6; N, 10·7. $C_{18}H_{14}N_2$ requires C, 83·7; H, 5·4; N, 10·8%).

1 : 9-*Phenylenecarbazole*.—To a solution of 1-amino-9-phenylcarbazole (0·33 g.) in glacial acetic acid (3·5 ml.), concentrated sulphuric acid (0·7 ml.) was added, followed by a solution of sodium nitrite (0·09 g.) in water (2 ml.). The colour of the paste changed from brown to red. After 15 minutes the mixture was gently warmed until effervescence ceased; it was finally boiled for 15 minutes. The material which separated on cooling was washed with dilute acetic acid (1 : 1), then with water, dried, and extracted with ethanol. The product (0·25 g.) obtained by concentration was sublimed in a vacuum and crystallised from methanol–acetone (2 : 1). The needles obtained had the characteristic appearance of 1 : 9-phenylenecarbazole (0·11 g.; yield, 36%), m. p. 136·5—138·5° (corr.), alone or mixed with a specimen synthesised by Dunlop and Tucker's method.

The following were prepared for comparison with the above: 3-*Nitro*-9-*phenylcarbazole* was prepared as 1-nitro-9-phenylcarbazole, above. Extraction with hot benzene, followed by crystallisation from methanol–benzene (1 : 2), gave yellow rosettes, m. p. 140—142° (1·8 g.; yield, 44%) (Found: C, 75·1; H, 4·2; N, 9·7. $C_{18}H_{12}O_2N_2$ requires C, 75·0; H, 4·2; N, 9·7%).

9-(2′-*Aminophenyl*)*carbazole* (Dunlop and Tucker, *loc. cit.*, p. 1950).—This was obtained by reduction of 9-(2′-nitrophenyl)carbazole in a manner similar to that used above for 1-amino-9-phenylcarbazole. Crystallisation from ethanol took place extremely slowly: an improvement was effected by boiling the crude amine (yield ~75%) in methanol solution with a few shavings of magnesium, and, after filtration, keeping the solution in a refrigerator for several days.

We thank the Carnegie Trustees for the award of a Research Scholarship (to R. W. G. P.); and Mr. J. M. L. Cameron for carrying out micro-analyses.

THE UNIVERSITY, GLASGOW. [*Received, June 30th*, 1943.]

# NOTES.

*Note on the Co-ordination Number of Bivalent Lead.* By R. COLIN HAWORTH and FREDERICK G. MANN.

THIOUREA is known to co-ordinate very readily with many metallic salts, giving derivatives of comparatively high stability; it is of value, therefore, in that a metallic atom may show a higher co-ordination valency when linked to thiourea than when linked to many other organic molecules. Rosenheim and Meyer (*Z. anorg. Chem.*, 1906, **49**, 18) described a thiourea–lead nitrate compound to which they ascribed the unlikely composition $11CS(NH_2)_2,2Pb(NO_3)_2$. We have had occasion to repeat this preparation: the *compound* crystallises from water in colourless needles, m. p. 160° (decomp.), and has the composition $6CS(NH_2)_2,Pb(NO_3)_2$. Molecular-weight determinations show that the salt undergoes considerable dissociation in boiling dilute aqueous solution, from which, however, it crystallises unchanged again on cooling. If the six thiourea molecules are co-ordinated normally to the lead atom, giving a salt, $[\{CS(NH_2)_2\}_6Pb](NO_3)_2$, the lead has now the electronic state of uranium. It is possible that the thiourea molecules are not, however, co-ordinated to the lead, and that the substance is a "molecular addition compound:" this could be decided only by *X*-ray crystal analysis.

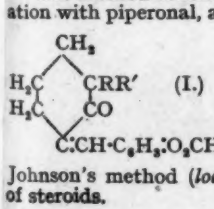
*Preparation.*—Solutions of lead nitrate (3 g.) and thiourea (4·5 g., 6·5 mols.) in hot water (10 c.c. and 15 c.c.) are mixed and cooled. The white crystals which separate are collected, and recrystallised from water; m. p. 160° (decomp.) (Found: C, 9·3; H, 3·0; N, 24·9; S, 24·0; Pb, 26·5; *M*, micro-ebullioscopic in 0·81% aqueous solution, 79; in 1·45% solution, 79; in 2·004% solution, 82; in 4·962% solution, 96. $C_6H_{24}O_6N_{14}S_6Pb$ requires C, 9·1; H, 3·0; N, 24·9; S, 24·4; Pb, 26·3%; *M*, 787). The above composition was confirmed by analysis of several preparations.

It is the possible formation of similar compounds that renders necessary the use of excess of litharge in the preparation of dicyandiamide from thiourea (Haworth and Mann, this vol., p. 606).—UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, September 29th*, 1943.]

*Preparation of Derivatives of* 2 : 2-*Dialkylcyclohexanone*. By ARTHUR J. BIRCH.

IN view of Johnson's publication (*J. Amer. Chem. Soc.*, 1943, **65**, 1317) on the direct introduction of angular methyl groups, it seems advisable to place on record some preliminary experiments along the same lines carried out in 1940, and included in Birch, D.Phil. Thesis, Oxford, 1940.

The method consists in the protection of the methylene group in the 6-position of a 2-alkyl*cyclo*hexanone by condensation with piperonal, and alkylation of the product by means of sodamide and an alkyl halide, thus forcing the formation of a quaternary carbon atom. 6-*Piperonylidene*-2-*methyl*cyclo*hexanone* (I; R = Me, R′ = H) was methylated to 2 : 2-*dimethyl*-, and ethylated to 2-*methyl*-2-*ethyl*-6-*piperonylidene*cyclo*hexanone* (I; R = Me, R′ = Me and Et respectively). The constitution of the former was proved by its formation from 2 : 2-dimethyl*cyclo*hexanone and piperonal. Although a similar type of methylation was carried out by Koebner and Robinson (J., 1941, 566), the structure of the product was not rigidly proved. By analogy with the above alkylations it is evident that the products obtained by these authors are correctly formulated, so, in conjunction with Johnson's method (*loc. cit.*) for removing the arylidene group, the method should prove of great value in the synthesis of steroids.



(I.)

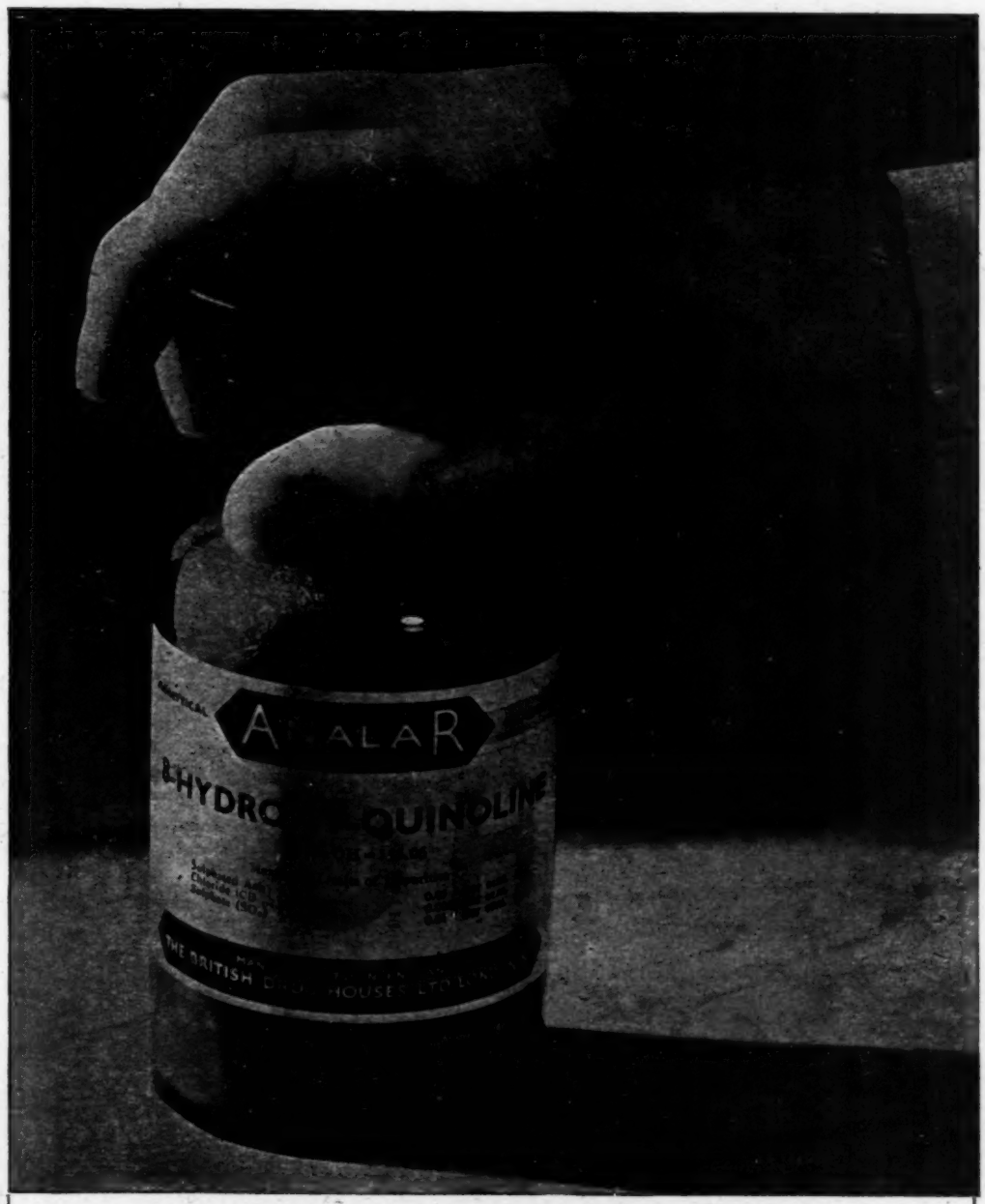
6-*Piperonylidene*-2-*methyl*cyclo*hexanone*.—Piperonal (32 g.), 2-methyl*cyclo*hexanone (27 g.), and a solution of sodium (0·5 g.) in alcohol (100 c.c.) were mixed, left for 4 days, and poured into water. The product was extracted with ether and recovered as a pale yellow resin, b. p. 230—245°/13 mm., which crystallised in contact with alcohol. Recrystallised from a small volume of the same solvent, it formed pale yellow prisms (17 g.), m. p. 74—75° (Found: C, 73·6; H, 6·5. $C_{15}H_{16}O_3$ requires C, 73·8; H, 6·6%).

6-*Piperonylidene*-2 : 2-*dimethyl*cyclo*hexanone*.—(I) The above product (10 g.) in toluene (50 c.c.) was refluxed with finely powdered sodamide (1·7 g.) for 90 minutes, and methyl iodide (8 g.) added, heating being continued for a further hour. The mixture was cooled and poured into water, the product collected in a little ether, and the solvent removed. The residue crystallised from a little alcohol in pale yellow, flat needles (8 g.), m. p. 67°, which considerably depressed the m. p. of the starting material (Found: C, 74·4; H, 7·0. $C_{16}H_{18}O_3$ requires C, 74·4; H, 7·0).

(II) 2 : 2-Dimethyl*cyclo*hexanone (25 g.) (Adamson, Marlow, and Simonsen, J., 1938, 774) and powdered sodamide (5 g.) were refluxed in benzene (50 c.c.) until the evolution of ammonia ceased, and piperonal (30 g.) was added to the ice-cooled solution. After washing with water, the product was worked up in the usual manner, being obtained as a yellow resin, b. p. 230—245°/10 mm., which crystallised from alcohol in pale yellow, flat prisms, m. p. 67°, undepressed by the sample obtained by method (I).

6-*Piperonylidene*-2-*methyl*-2-*ethyl*cyclo*hexanone*.—6-Piperonylidene-2-methyl*cyclo*hexanone (7 g.) in benzene (20 c.c.) was treated as above with sodamide (1·1 g.) and ethyl iodide (5 g.). The product boiled at 245°/10 mm., and crystallised from an equal volume of alcohol in cream-coloured plates (4·5 g.), m. p. 60—61° (Found: C, 74·9; H, 7·4. $C_{17}H_{20}O_3$ requires C, 75·0; H, 7·3%).

The author wishes to thank the Royal Commissioners for the Exhibition of 1851 for an overseas scholarship.—Dyson Perrins Laboratory, Oxford University. [*Received, August 23rd*, 1943.]



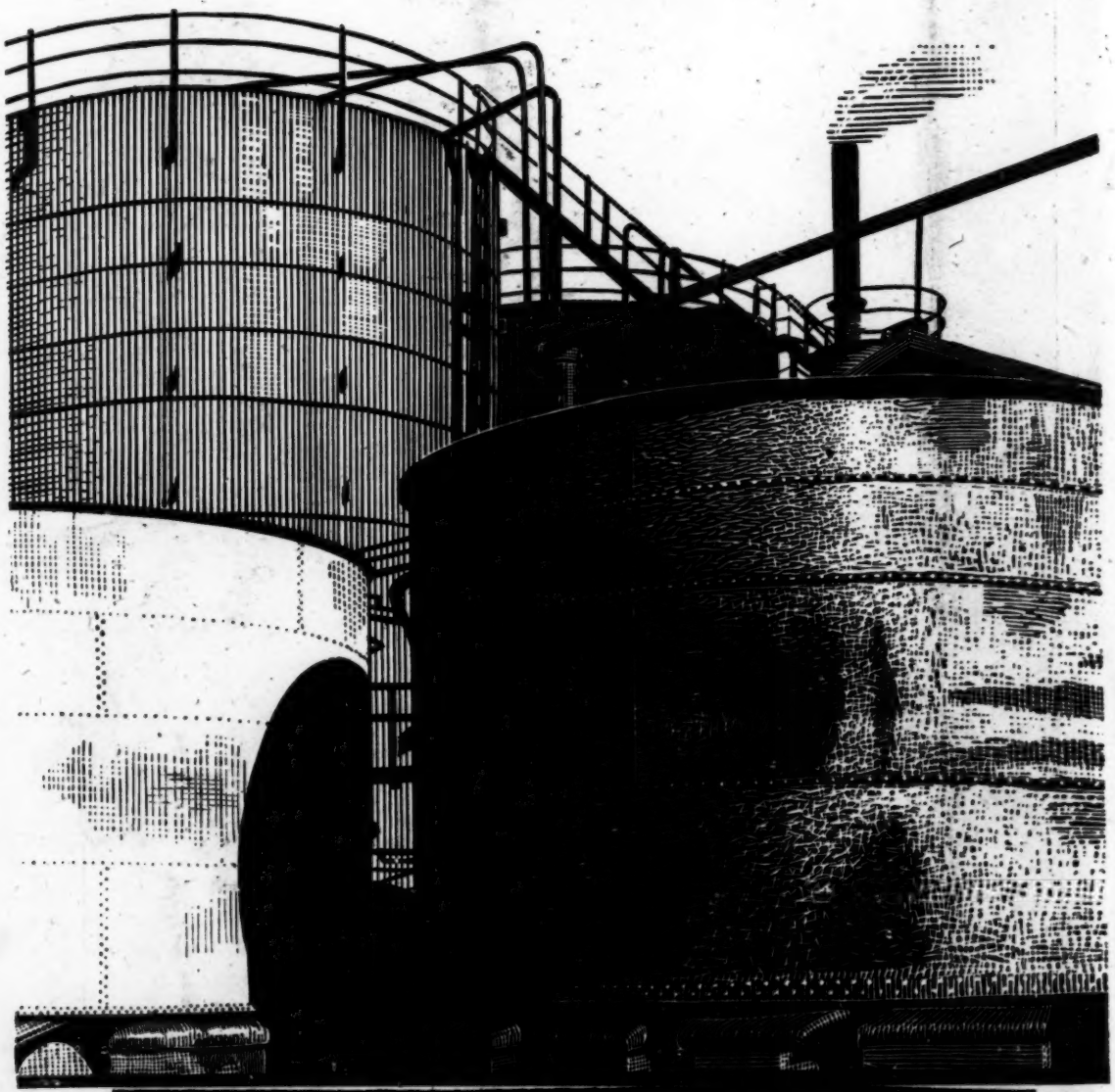

*Reagents of 'AnalaR' quality are guaranteed to conform to the specifications published in the book of "'AnalaR' Standards for Laboratory Chemicals."*

*All inquiries should be addressed to*
*The British Drug Houses, Ltd., Graham Street, London, N.1.*

**THE BRITISH DRUG HOUSES LTD**

"Staybrite"
REG. TRADE MARK
SUPER RUSTLESS STEEL

FOR ALL TYPES OF CHEMICAL PLANT



FIRTH-VICKERS STAINLESS STEELS LTD SHEFFIELD

PRINTED IN GREAT BRITAIN BY RICHARD CLAY AND COMPANY, LTD. BUNGAY, SUFFOLK

# INDEX OF AUTHORS, 1943.


A.

**Adamson,** *D. W.*, anhydrides of basic amino-acids, 39.
**Addison,** *C. C.*, properties of freshly formed surfaces. Part I. Application of the vibrating-jet technique to surface-tension measurements on mobile liquids, 535.
**Albert,** *A.*, and **Goldacre,** *R.*, nature of the amino-group in aminoacridines. Part I. Evidence from electrometric studies, 454.
**Albert,** *A.*, **Goldacre,** *R.*, and **Heymann,** *E.*, aminoacridines; partition and surface phenomena, 651.
**Albert,** *A.*, and **Ritchie,** *B.*, nature of the amino-group in aminoacridines. Part II. Evidence from chemical reactions, 458.
**Anderson,** *J. S.*, vapour pressure of metallic indium, 141.
**Anderson,** *J. S.*, **Briscoe,** *H. V. A.*, **Cobb,** *L. H.*, and **Spoor,** *N. L.*, interchange of hydrogen isotopes with complex salts. Part II. Kinetics of interchange with platinous and palladous tetrammines, 367.
**Anderson,** *J. S.*, **Briscoe,** *H. V. A.*, and **Spoor,** *N. L.*, interchange of hydrogen isotopes with complex salts. Part I. Kinetics of interchange with the luteocobaltic complex, 361.
**Angus,** *W. R.*, and **Owen,** *R. P.*, stability of racemates; mandelic acid and some of its derivatives, 227.
aqueous solubilities of *r*- and *l*-mandelic acids and three *o*-acyl-*r*-mandelic acids, 231.
effect of heat on mandelic acid, 249.
**Atherton,** *D.*, and **Hilditch,** *T. P.*, stereochemical relationships of 9 : 10-oxidostearic acids and 9 : 10-dihydroxystearic acids, 204.
**Azzam,** *R. C.* See **Zaki,** *A.*

B.

**Backeberg,** *O. G.*, and **Marais,** *J. L. C.*, 5-acetamidosaccharin, a derivative of sulphanilamide, 78.
**Baddeley,** *G.*, Fries rearrangement and subsequent isomerisation, 273.
action of aluminium chloride on phenol homologues, 527.
**Baddeley,** *G.*, and **Plant,** *J.*, action of aluminium chloride on aromatic bromo-compounds, 525.
**Baddiley,** *J.*, **Lythgoe,** *B.*, **McNeil,** *D.*, and **Todd,** *A. R.*, experiments on synthesis of purine nucleosides. Part I. Synthesis of 9-alkylpurines, 383.
**Baddiley,** *J.*, **Lythgoe,** *B.*, and **Todd,** *A. R.*, experiments on synthesis of purine nucleosides. Part II. Synthesis of adenine. Part III. 4-Glycosidaminopyrimidines, 386, 571.
**Baker,** *W.*, **Grice,** *K. D.*, and **Jansen,** *A. B. A.*, synthesis of α-acyltetronic acids, 241.
**Baker,** *W.*, and **McGowan,** *J. C.*, condensation products of phenols and ketones. Part VI. Conversion of an *o*-quinone into a derivative of pyrogallol, 486.
**Balfe,** *M. P.*, **Hills,** *H. W. J.*, **Kenyon,** *J.*, **Phillips,** *H.*, and **Platt,** *B. C.*, optically active αγ-dimethylallyl alcohols, 348.
**Balfe,** *M. P.*, **Kenyon,** *J.*, and **Tárnoky,** *A. L.*, alkyl–oxygen fission in sulphinic esters, 446.
**Bance,** *S.*, **Barber,** *H. J.*, and **Woolman,** *A. M.*, bromination of diphenylalkanes and preparation of stilbene derivatives. Part I. αβ-Diphenylethane, 1.
**Barber,** *H. J.*, cuprous cyanide : preparation and use, 79.
some sulphonyl derivatives of amidines and imino-ethers, 101.
**Barber,** *H. J.*, **Slack,** *R.*, and **Woolman,** *A. M.*, bromination of diphenylalkanes and preparation of stilbene derivatives. Part II. βγ-Diphenyl-*n*-butane, 99.
**Barber,** *H. J.* See also **Bance,** *S.*
**Barker,** *G. R.* See **Gulland,** *J. M.*
**Barton,** *D. H. R.*, and **Jones,** *E. R. H.*, studies in the sterol group. Part XLV. Investigation of the homogeneity of sitosterol by oxidation with the Oppenauer reagent. Part XLVI. Isolation of a new form of $\Delta^4$-cholestenone, 599, 602.
**Baxter,** *R. A.*, and **Spring,** *F. S.*, β-cholesterol oxide, 613.
**Belcher,** *R.*, and **Spooner,** *C. E.*, technique for ultimate microanalysis of organic compounds, 313.
**Bell,** *R. P.*, recent advances in the theory of reaction kinetics in solution, 629.
**Bell,** *R. P.* See also **Longuet-Higgins,** *H. C.*
**Bennett,** *D. J.*, **Pritchard,** *R. R.*, and **Simonsen,** *J. L.*, dinitrodibenzanthrone, 31.
**Bergel,** *F.*, and **Morrison,** *A. L.*, oxidation of adrenaline, 48.
5-hydroxyindole, 49.
**Bergel,** *F.*, **Morrison,** *A. L.*, **Rinderknecht,** *H.*, **Todd,** *A. R.*, **Macdonald,** *A. D.*, and **Woolfe,** *G.*, *Cannabis indica*. Part XII. Some analogues and a water-soluble derivative of tetrahydro-cannabinol, 286.
**Berkeley,** (*Earl of*), obituary notice of, 503.
**Birch,** *A. J.*, preparation of derivatives of 2:2-dialkylcyclohexanone, 661.
**Birch,** *A. J.*, and **Robinson,** (*Sir*) *R.*, β-alkylation of kationoid systems by means of Grignard reagents, 501.
**Bird,** (*Miss*) *M. L.*, **Hughes,** *E. D.*, and **Ingold,** *C. K.*, mechanism of reaction between alkyl halides and hydroxylic solvents. Part III. Reactions of *n*-butyl bromide, 255.
**Birtwell,** *S.* See **Hodgson,** *H. H.*
**Blagden,** *J. W.*, obituary notice of, 334.
**Bloomfield,** *G. F.*, rubber, polyisoprenes, and allied compounds. Part IV. Relative tendencies towards substitutive and additive reaction during chlorination, 289.
autoxidation reactions in polyisoprene and allied compounds. Part III. Oxidation of rubber in presence of acetic acid or acetic anhydride, 356.
**Boon,** *A. A.*, obituary notice of, 507.
**Briggs,** *L. H.*, and **Lyttleton,** *J. W.*, reactions of hydrazoic acid. Part II. Quantitative study of the action with substituted benzoic acids, 421.
**Briscoe,** *H. V. A.* See **Anderson,** *J. S.*
**Bromby,** *N. G.*, **Peters,** *A. T.*, and **Rowe,** *F. M.*, butylnaphthalenes and their derivatives. Part I. β-*tert*.-Butylnaphthalene, 144.
**Buchanan,** *C.*, **Loudon,** *J. D.*, and **Robertson,** *J.*, 4-nitro-3-ethoxytoluene-6-sulphonic acid, 168.
**Buchanan,** *J.*, **Percival,** *E. E.*, and **Percival,** *E. G. V.*, polysaccharides of carragheen moss (*Chondrus crispus*). Part I. Linkage of the *d*-galactose residues and the ethereal sulphate, 51.
**Bulcraig,** *W. R.*, and **Dawson,** *H. M.*, kinetics of aqueous hydrolysis of sodium phenylbromoacetate and sodium phenylchloroacetate, 80.
**Burt,** (*Sir*) *B. C.*, obituary notice of, 200.
**Burton,** *H.*, and **Walker,** *N.*, complex-formation and rearrangement of *p*-hydroxylaminobenzenesulphonamide, 656.

C.

**Chatt,** *J.*, and **Wynne,** *W. P.*, 1:3:5:7-tetranitronaphthalene and the isomeric tetranitro-derivatives obtained from 2:6-dinitronaphthalene by nitration, 33.
**Clifford,** *F. W.*, obituary notice of, 201.
**Coates,** *H.*, **Cook,** *A. H.*, **Heilbron,** *I. M.*, **Hey,** *D. H.*, **Lambert,** *A.*, and **Lewis,** *F. B.*, new therapeutic agents of the quinoline series. Introduction and Part I. Monopyridylquinolines. Part III. Methoxy-, hydroxy-, and alkyl-pyridylquinolines. 401, 406.
**Coates,** *H.*, **Cook,** *A. H.*, **Heilbron,** *I. M.*, and **Lewis,** *F. B.*, new therapeutic agents of the quinoline series. Part VI. Quinolyl-thiazoles, -amidines, and -pyrroles, 419.
**Cobb,** *J. W.* See **Milner,** *G.*
**Cobb,** *L. H.* See **Anderson,** *J. S.*
**Cocker,** *W.*, hydroxyalkylamino-acids. Part I., 373.
**Connolly,** *E. E.*, condensation products of acetaldehyde, 42.

**Cook**, *A. H.*, **Heilbron**, *I. M.*, **Hey**, *D. H.*, **Lambert**, *A.*, and **Spinks**, *A.*, new therapeutic agents of the quinoline series. Part II. Dipyridylquinolines, 404.

**Cook**, *A. H.*, **Heilbron**, *I. M.*, and **Spinks**, *A.*, new therapeutic agents of the quinoline series. Part V. Pyridylacridines, 417.

**Cook**, *A. H.*, **Heilbron**, *I. M.*, and **Steger**, *L.*, new therapeutic agents of the quinoline series. Part IV. Lutidylquinolines, 413.

**Cook**, *A. H.*, and **Naylor**, *R. F.*, quinoxaline cyanines. Part III., 397.

**Cook**, *A. H.*, and **Perry**, *C. A.*, quinoxaline cyanines. Part II., 394.

**Cook**, *A. H.* See also **Coates**, *H.*

**Cooke**, *P. W.* See **Powell**, *H. M.*

**Cornforth**, *J. W.*, **Cornforth**, (*Mrs.*) *R. H.*, and **Robinson**, (*Sir*) *R.*, nuclear methylation of α-naphthol, 168.

**Cornforth**, (*Mrs.*) *R. H.* See **Cornforth**, *J. W.*

**Cowan**, *D. M.* See **Vogel**, *A. I.*

**Cripps**, *R. W.*, and **Hey**, *D. H.*, nuclear alkylation of aromatic bases. Part V. Action of methyl alcohol on *m*-toluidine hydrochloride, 14.

**Crouch**, *E. A. C.* See **Hodgson**, *H. H.*

**Crowther**, *A. F.*, **Mann**, *F. G.*, and **Purdie**, *D.*, mechanism of indole formation from phenacylarylamines. Part I., 58.

**Crum**, (*Miss*) *J.*, and **Robinson**, (*Sir*) *R.*, attempts to find new antimalarials. Part XX., 561.

**Cunneen**, *J. I.*, **Farmer**, *E. H.*, and **Koch**, *H. P.*, rubber, polyisoprenes and allied compounds. Part V. Chemical linking of rubber and of other olefins with phenol–formaldehyde resins, 472.

**Curtis**, *E. G.* See **Irving**, *H.*

D.

**Davies**, *R. R.*, and **Hodgson**, *H. H.*, catalytic reduction by formic acid under pressure. Part I. Preparation of aldehydes from carboxylic acids with titanium dioxide as catalyst. Part II. Comparison of copper and nickel as catalysts, 84, 281.

catalytic dehydrogenation of alcohols to aldehydes in the presence of air, 282.

**Dawson**, *H. M.*, **Pycock**, *E. R.*, and **Smith**, *G. F.*, elimination of chlorine from sodium chloroacetate by salts of weak acids, 517.

**Dawson**, *H. M.* See also **Bulcraig**, *W. R.*

**De la Mare**, *P. B. D.*, and **Robertson**, *P. W.*, kinetics of aromatic halogenation. Part II. Chlorination of hydrocarbons, 279.

**De la Mare**, *P. B. D.* See also **Robertson**, *P. W.*

**Dufton**, *S. F.*, obituary notice of, 508.

E.

**Egan**, (*Miss*) *D. M.*, and **Partington**, *J. R.*, activity coefficients of zinc chloride, bromide, and iodide from electromotive forces, 157.

**Elks**, *J.*, and **Hey**, *D. H.*, β-3:4-methylenedioxyphenyl*iso*propylamine, 15.

union of aryl nuclei. Part VI. Reactions with 1-aryl-3:3-dimethyltriazens, 441.

**Evans**, *L. K.*, and **Gillam**, *A. E.*, effect of molecular environment on absorption spectra of organic compounds in solution. Part III. Compounds containing the chromophore $>C{=}C{-}C{=}N-$, 565.

**Ewen**, *E. S.*, and **Spring**, *F. S.*, triterpene resinols and related acids. Part XIV. Oxidation of acetylursolic acid, 523.

F.

**Farmer**, *E. H.*, **Koch**, *H. P.*, and **Sutton**, *D. A.*, autoxidation reactions in polyisoprenes and allied compounds. Part VII. Rearrangement of double bonds during autoxidation, 541.

**Farmer**, *E. H.*, and **Sundralingam**, *A.*, autoxidation reactions in polyisoprenes and allied compounds. Part VI. Peroxidation of rubber, 125.

**Farmer**, *E. H.*, and **Sutton**, *D. A.*, autoxidation reactions in polyisoprenes and allied compounds. Part IV. Isolation and constitution of photochemically-formed methyl oleate. Part V. Fish-oil acids, 119, 122.

**Farmer**, *E. H.* See also **Cunneen**, *J. I.*

**Fisk**, *P. M.*, and **Pollak**, *F. F.*, volumetric method for determination of lead in brass, 41.

G.

**Gibling**, *T. W.*, molecular volume and structure. Parts V. and VI., 146.

**Gillam**, *A. E.* See **Evans**, *L. K.*

**Given**, *P. H.*, free energy of methyl ether from the methanol-methyl ether equilibrium $2MeOH(v.) = Me_2O + H_2O(v.)$, 589.

**Glen**, *W. L.*, and **Robinson**, (*Sir*) *R.*, attempts to find new antimalarials. Part XIX., 557.

**Goldacre**, *R.* See **Albert**, *A.*

**Goldberg**, *A. A.*, taurine, 4.

**Goodson**, *J. A.*, alkaloids of the seeds of *Delphinium elatum*, L., 139.

**Granichstädten**, *H.*, and **Percival**, *E. G. V.*, polysaccharides of Iceland moss (*Cetraria islandica*). Part I. Hemicelluloses, 54.

**Gregg**, *S. J.*, heat of adsorption of ethyl chloride and of sulphur dioxide on sugar charcoal, 351.

**Grice**, *K. D.* See **Baker**, *W.*

**Gulland**, *J. M.*, and **Barker**, *G. R.*, constitution of yeast ribonucleic acid. Part VI. Nature of the carbohydrate radicals, 625.

H.

**Hamer**, (*Miss*) *F. M.*, and **Rathbone**, *R. J.*, thiazinocyanines. Part II. Cyanines containing the dihydro-1:3-thiazine nucleus. Part III. Carbocyanines containing the *peri*-naphtha-1:3-thiazine nucleus, 243, 487.

**Harbord**, *F. W.*, obituary notice of, 202.

**Harden**, *A.*, obituary notice of, 334.

**Harrison**, *W. S. W.*, **Peters**, *A. T.*, and **Rowe**, *F. M.*, polyhalogeno-*o*-anisidines and their derivatives, 235.

**Hart**, *A. B.*, and **Partington**, *J. R.*, dissociation pressures of compounds of ammonia and trideuterammonia with metallic salts, 104.

**Hatt**, *H. H.*, and **Stephenson**, (*Miss*) *E. F. M.*, heterocyclic nitrogen compounds. Part I. Derivatives of 7:16-diazonaphthacene, 658.

**Haward**, *R. N.* See **White**, *T.*

**Haworth**, *R. C.*, and **Mann**, *F. G.*, properties of urea, biuret, and triuret, 603.

co-ordination number of bivalent lead, 661.

**Haworth**, *R. D.*, **Jones**, *B.*, and **Way**, (*Miss*) *Y. M.*, synthesis of 4-hydroxy-2-naphthoic acids, 10.

**Haworth**, *W. N.*, **Kitchen**, *H.*, and **Peat**, *S.*, amylolytic degradation of starch, 619.

**Heilbron**, *I. M.*, **Johnson**, *A. W.*, **Jones**, *E. R. H.*, and **Raphael**, *R. A.*, studies in the polyene series. Part X. Condensation of 3-methylpent-2-en-4-yne (1:2-dimethylvinylacetylene) with butaldehyde, crotonaldehyde, and citral; anionotropic rearrangements with vinylacetylenecarbinols derived from αβ-unsaturated aldehydes, 265.

**Heilbron**, *I. M.*, **Jones**, *E. R. H.*, and **Raphael**, *R. A.*, studies in the polyene series. Part IX. Condensation product of 1-hexyne with crotonaldehyde and its anionotropic rearrangement. Part XI. Anionotropic rearrangement of the acetylenic glycol from crotonaldehyde, 264, 268.

**Heilbron**, *I. M.* See also **Coates**, *H.*, and **Cook**, *A. H.*

**Hey**, *D. H.* See **Coates**, *H.*, **Cook**, *A. H.*, **Cripps**, *R. W.*, and **Elks**, *J.*

**Heymann**, *E.* See **Albert**, *A.*

**Hickling**, *A.*, and **Rodwell**, *F.*, studies in electrolytic oxidation. Part XIII. Electrolytic oxidation of formaldehyde, 90.

**Hilditch**, *T. P.* See **Atherton**, *D.*

**Hills**, *H. W. J.* See **Balfe**, *M. P.*

**Hinshelwood**, *C. N.* See **Lodge**, *R. M.*

**Hobday**, *G. I.*, and **Short**, *W. F.*, dienœstrol, 609.

**Hodgson**, *H. H.*, tautomerism of benzoquinone-*p*-nitrosophenol systems. Part II. 3-Fluoro-4-nitrosophenol, 89.
absorption spectra of *m*-substituted phenols, and influence of nucleophilic substituents on electronic mobility, 380.
**Hodgson**, *H. H.*, and **Birtwell**, *S.*, preparation of diazo-naphthols and nitration of 4-bromoaceto-1-naphthalide, 321.
preparation of 1:3-dinitronaphthalene, 433.
preparation of 4-halogeno-2-naphthols and 4-nitro-2-naphthol, with resonance structure of the internal diazo-oxides (diazo-naphthols), 468.
**Hodgson**, *H. H.*, and **Crouch**, *E. A. C.*, nitrosation of phenols. Part XIX. Three cresols and their methyl ethers; semicarbazide reactions, 221.
**Hodgson**, *H. H.*, and **Marsden**, *E.*, *N*-nitrosoaceto-1-naphthalide, 285.
decomposition of diazo-compounds in neutral solution; diazo-coupling reaction, 379.
sulphite and sulphonate structures of Hantzsch's potassium benzene-*syn*- and -*anti*-diazosulphonates, 470.
**Hodgson**, *H. H.*, and **Turner**, *H. S.*, action of cuprous oxide on diazotised amines. Part II. Reactions in solutions of various alcohols and organic solvents; preparation of 1:6-dinitronaphthalene, 86.
monoreduction of dinitronaphthalenes in acid solution and of 1:5- and 1:6-dinitronaphthalene by aqueous sodium sulphide, 318.
influence of the 6-nitro-group on the halogenation, nitration, mercuration, and diazo-coupling of 6-nitro-1-naphthylamine and of related naphthalides, 391.
preparation of 2:3-dinitronaphthalene and of 3-nitro-2-naphthylamine, 635.
**Hodgson**, *H. H.* See also **Davies**, *R. R.*
**Holliman**, *F. G.*, and **Mann**, *F. G.*, synthetic application of *o*-*β*-bromoethylbenzyl bromide. Part II. Preparation and properties of 2-substituted 1:2:3:4-tetrahydro*iso*arsinolines. Part III. Preparation and optical resolution of 2-phenyl-2-*p*-chlorophenacyl-1:2:3:4-tetrahydro*iso*arsinolinium bromide, 547, 550.
**Hughes**, *E. D.* See **Bird**, (*Miss*) *M. L.*
**Hunter**, *M.*, obituary notice of, 43.
**Huse**, *G.* See **Powell**, *H. M.*
**Hutchinson**, *A.*, obituary notice of, 340.

I.

**Ingold**, *C. K.* See **Bird**, (*Miss*) *M. L.*
**Irving**, *H.*, and **Curtis**, *E. G.*, action of alkalis on substituted benzdioxins, 319.
**Iskander**, *Y.* See **Zaki**, *A.*
**Ives**, *D. J. G.*, and **Sames**, *K.*, determination of dissociation constants of monobasic acids. Part II. Extrapolation method. Part III. Strengths of cyano-acids, 511, 513.

J.

**Jansen**, *A. B. A.* See **Baker**, *W.*
**Johnson**, *A. W.* See **Heilbron**, *I. M.*
**Johnston**, *W. T. G.* See **Robertson**, *P. W.*
**Jones**, *B.*, halogenation of phenolic ethers and anilides. Part XIV. *m*-Substituted phenyl ethers, 430.
ethers of 4-chloro-2-nitro-3:5-dimethylphenol, 445.
**Jones**, *B.* See also **Haworth**, *R. D.*
**Jones**, *E. R. H.*, and **McCombie**, *J. T.*, studies in the polyene series. Part VIII. A new anionotropic rearrangement; isomerisation of ethynylcarbinols from *αβ*-unsaturated aldehydes, 261.
**Jones**, *E. R. H.* See also **Barton**, *D. H. R.*, and **Heilbron**, *I. M.*

K.

**Kenner**, *G. W.*, **Lythgoe**, *B.*, **Todd**, *A. R.*, and **Topham**, *A.*, reactions of amidines with derivatives of malonic acid, 388.
experiments on synthesis of purine nucleosides. Part IV. 4:6-Diaminopyrimidine; synthesis of pyrimidine derivatives, 574.
**Kenyon**, *J.* See **Balfe**, *M. P.*
**King**, *G.*, mechanism of oxidation of oleic and elaidic acids and their methyl esters by hydrogen peroxide in acetic acid; configurations of the 9:10-dihydroxystearic acids, 37.
**Kitchen**, *H.* See **Haworth**, *W. N.*
**Koch**, *H. P.* See **Cunneen**, *J. I.*, and **Farmer**, *E. H.*

L.

**Lamb**, *I. D.*, obituary notice of, 202.
**Lambert**, *A.* See **Coates**, *H.*, and **Cook**, *A. H.*
**Leitch**, (*Miss*) *G. C.*, obituary notice of, 341.
**Lewis**, *F. B.* See **Coates**, *H.*
**Lloyd**, *D. J.*, and **Pugh**, *W.*, gallium. Part VI. Separation of gallium and germanium from alkaline extracts of germanite by electrolysis. Part VII. Gallium perchlorate hydrates and a gallium perchlorate–urea complex, 74, 76.
**Lodge**, *R. M.*, and **Hinshelwood**, *C. N.*, physicochemical aspects of bacterial growth. Part VIII. Growth of *Bact. lactis aerogenes* in media containing ammonium sulphate or various amino-acids. Part IX. Lag phase of *Bact. lactis aerogenes*. Part X. Variability of growth rate of *Bact. lactis aerogenes*, 208, 213, 219.
**Longuet-Higgins**, *H. C.*, and **Bell**, *R. P.*, structure of boron hydrides, 250.
**Loudon**, *J. D.* See **Buchanan**, *C.*
**Lynas-Gray**, *J. I.*, and **Simonsen**, *J. L.*, action of bases on 1-diazoanthraquinone-2-sulphonate and its derivatives, 45.
**Lythgoe**, *B.* See **Baddiley**, *J.*, and **Kenner**, *G. W.*
**Lyttleton**, *J. W.* See **Briggs**, *L. H.*

M.

**McCombie**, *J. T.* See **Jones**, *E. R. H.*
**Macdonald**, *A. D.* See **Bergel**, *F.*
**McGowan**, *J. C.* See **Baker**, *W.*
**McIlwain**, *H.*, bacterial inhibition by metabolite analogues. Part V. Reactions and antibacterial properties of *p*-diazine di-*N*-oxides, 322.
**McNeil**, *D.* See **Baddiley**, *J.*
**Mann**, *F. G.*, and **Watson**, *J.*, preparation and properties of poly-sulphanilamide compounds, 606.
**Mann**, *F. G.* See also **Crowther**, *A. F.*, **Haworth**, *R. C.*, and **Holliman**, *F. G.*
**Marais**, *J. L. C.* See **Backeberg**, *O. G.*
**Marsden**, *E.* See **Hodgson**, *H. H.*
**Marsden**, *H.*, obituary notice of, 341.
**Marsh**, *J. K.*, rare-earth metal amalgams. Part III. Separation of ytterbium from its neighbours. Part IV. Isolation of europium, 8, 531.
yttrium-group oxalates, 40.
rare earths in scheelite, 577.
**Martin**, *R. H.*, polymethylbenzoylnaphthoic acids, 239.
**Martin**, *R. H.*, and **Robinson**, (*Sir*) *R.*, experiments on synthesis of substances related to the sterols. Part XLI. Androstenedione. Part I. Part XLII., 491, 497.
**Mellor**, *J. W.*, obituary notice of, 341.
**Miller**, *C. C.*, qualitative semimicro-analysis with reference to Noyes and Bray's system; aluminium group, 72.
**Mills**, *W. H.*, stereochemistry of labile compounds, 194.
**Milner**, *G.*, **Spivey**, *E.*, and **Cobb**, *J. W.*, the solid product of carbonisation, 578.
**Morrison**, *A. L.* See **Bergel**, *F.*
**Morrison-Jones**, *C. R.*, obituary notice of, 343.
**Morton**, *R. A.* See **Simpson**, *J. C. E.*
**Mostafa**, *A.* See **Schönberg**, *A.*
**Moubacher**, *R.* See **Schönberg**, *A.*
**Mustafa**, (*Miss*) *A.* See **Schönberg**, *A.*
**Mustafa**, (*Miss*) *Z.*, and **Soliman**, *G.*, melanthigenin and its identity with hederagenin, 70.

N.

**Naylor**, *R. F.* See **Cook**, *A. H.*
**Niekerk**, *J. N. van.* See **Rapson**, *W. S.*

O.

**Odling**, *W.*, obituary notice of, 43.

**Owen**, *L. N.*, polymerisation of acetaldol, 445.
oxygenation of crotonaldehyde, 463.
**Owen**, *R. P.* See **Angus**, *W. R.*

P.

**Page**, *J. E.*, and **Robinson**, *F. A.*, polarographic studies. Part II. Mould metabolites and related quinones, 133.
**Paige**, *M. F. C.*, acyl migrations in the sterol series, 437.
**Partington**, *J. R.* See **Egan**, (*Miss*) *D. M.*, and **Hart**, *A. B.*
**Peak**, *D. A.*, and **Short**, *W. F.*, interconversion of hexœstrol and *iso*hexœstrol, 232.
**Peat**, *S.* See **Haworth**, *W. N.*
**Percival**, *E. E.* See **Buchanan**, *J.*
**Percival**, *E. G. V.* See **Buchanan**, *J.*, and **Granichstädten**, *H.*
**Perry**, *C. A.* See **Cook**, *A. H.*
**Peters**, *A. T.*, **Rowe**, *F. M.*, and **Stead**, *D. M.*, derivatives of 1:2:4:5-tetrachlorobenzene. Part I. Nitro- and amino-compounds. Part II. *N*-Nitroamino-compounds. Part III. Amination of 2:3:5:6-tetrachloro-nitrobenzene and -4-nitro-aniline, 233, 372, 576.
**Peters**, *A. T.* See also **Bromby**, *N. G.*, and **Harrison**, *W. S. W.*
**Petrow**, *V. A.*, **Rosenheim**, *O.*, and **Starling**, *W. W.*, acyl migration in steroids, 135.
**Petrow**, *V. A.*, **Stack**, *M. V.*, and **Wragg**, *W. R.*, new syntheses of heterocyclic compounds. Part II. 2-Phenyl-3:4:6:7-dibenzo-1:5-naphthyridine, 316.
**Phillips**, *H.* See **Balfe**, *M. P.*
**Plant**, *J.* See **Baddeley**, *G.*
**Platt**, *B. C.* See **Balfe**, *M. P.*
**Polgar**, *N.*, and **Robinson**, (*Sir*) *R.*, long-chain acids containing a quaternary carbon atom. Part II., 615.
**Pollak**, *F. F.* See **Fisk**, *P. M.*
**Powell**, *H. M.*, and **Huse**, *G.*, structure of molecular compounds. Part II., 435.
**Powell**, *H. M.*, **Huse**, *G.*, and **Cooke**, *P. W.*, structure of molecular compounds. Part I. Crystal structure of *p*-iodo-aniline–*s*-trinitrobenzene, 153.
**Preston**, *R. W. G.*, and **Tucker**, *S. H.*, attempts to prepare optically active tervalent nitrogen compounds. Part II. 1:9-(2′:3′:4′:5′-Tetrahydrophenylene)carbazole, 659.
**Pritchard**, *R. R.* See **Bennett**, *D. J.*
**Pugh**, *W.* See **Lloyd**, *D. J.*
**Purdie**, *D.* See **Crowther**, *A. F.*
**Pycock**, *E. R.* See **Dawson**, *H. M.*

Q.

**Quin**, *D. C.*, and **Robinson**, (*Sir*) *R.*, attempts to find new antimalarials. Part XVIII., 555.

R.

**Raphael**, *R. A.* See **Heilbron**, *I. M.*
**Rapson**, *W. S.*, **Shuttleworth**, *R. G.*, and **Niekerk**, *J. N. van*, benz*cyclo*octatetraenes. Part III. Diphenylene and tetraphenylene, 326.
**Rathbone**, *R. J.* See **Hamer**, (*Miss*) *F. M.*
**Richardson**, (*Miss*) *M. F.*, and **Warren**, *F. L.*, *Senecio* alkaloids. Part I. Rosmarinine, 452.
**Rinderknecht**, *H.* See **Bergel**, *F.*
**Ritchie**, *B.* See **Albert**, *A.*
**Robertson**, *J.* See **Buchanan**, *C.*
**Robertson**, *P. W.*, **De la Mare**, *P. B. D.*, and **Johnston**, *W. T. G.*, kinetics of aromatic halogenation. Part I. Bromination, 276.
**Robertson**, *P. W.* See also **De la Mare**, *P. B. D.*
**Robinson**, *F. A.* See **Page**, *J. E.*
**Robinson**, (*Sir*) *R.* See **Birch**, *A. J.*, **Cornforth**, *J. W.*, **Crum**, (*Miss*) *J.*, **Glen**, *W. L.*, **Martin**, *R. H.*, **Polgar**, *N.*, and **Quin**, *D. C.*
**Rodwell**, *F.* See **Hickling**, *A.*
**Rogers**, *M. A. T.*, 2:4-diarylpyrroles. Part I. Synthesis of 2:4-diarylpyrroles and 2:2′:4:4′-tetra-arylazadipyrromethines. Part II. Methines. Part III. 3-Amino-2:4-diphenylpyrrole, 590, 596, 598.
**Rosenheim**, *O.* See **Petrow**, *V. A.*
**Rothstein**, *E.*, and **Saboor**, *M. A.*, influence of alkylation on reactions of acid derivatives in the Friedel–Crafts synthesis, 425.
**Rowe**, *F. M.* See **Harrison**, *W. S. W.*, and **Peters**, *A. T.*
**Rule**, *H. G.*, obituary notice of, 509.

S.

**Saboor**, *M. A.* See **Rothstein**, *E.*
**Sames**, *K.* See **Ives**, *D. J. G.*
**Schönberg**, *A.*, and **Mostafa**, *A.*, photo-reactions. Part V. Photo-oxidation of non-ionisable thioketones in sunlight. Part VI. Formation of benzpinacol by action of acetone on benzhydrol in sunlight, 275, 276.
the Diels–Alder synthesis with 2:3-dimethylquinoxaline; reaction between maleic anhydride and anthranil, 654.
**Schönberg**, *A.*, and **Moubacher**, *R.*, studies on indene derivatives. Part II. Triketohydrindene, 71.
**Schönberg**, *A.*, and **Mustafa**, (*Miss*) *A.*, action of phosphoric oxide on phenyl esters; mechanism of the Fries reaction, 79.
**Schönberg**, *A.* See also **Tadros**, *W.*
**Sharp**, *W.*, **Sutherland**, (*Miss*) *M. M. J.*, and **Wilson**, *F. J.*, preparation and therapeutic properties of acridine derivatives. Part III. 5-Styrylacridines and their quaternary salts. Part IV. 5-Methylacridines, further 5-styrylacridines and their quaternary salts, 5, 344.
**Short**, *W. F.* See **Hobday**, *G. I.*, and **Peak**, *D. A.*
**Shuttleworth**, *R. G.* See **Rapson**, *W. S.*
**Simonsen**, *J. L.* See **Bennett**, *D. J.*, and **Lynas-Gray**, *J. I.*
**Simpson**, *J. C. E.*, cinnolines. Part II. Influence of substituents on the Widman–Stoermer and the Pschorr reaction, 447.
**Simpson**, *J. C. E.*, and **Morton**, *R. A.*, the triterpene group. Part X., 477.
**Sinnatt**, *F. S.*, obituary notice of, 203.
**Slack**, *R.* See **Barber**, *H. J.*
**Slater**, *S. N.*, tutin, 50.
hydrogenation of tutin, 143.
**Smith**, *G. F.*, Brönsted relation in hydrolysis of the halogeno-acetates and the theory of acids and bases, 521.
**Smith**, *G. F.* See also **Dawson**, *H. M.*
**Soliman**, *G.* See **Mustafa**, (*Miss*) *Z.*
**Speakman**, *J. C.*, dissociation constants of acids in mixed solvents, 270.
**Spinks**, *A.* See **Cook**, *A. H.*
**Spivey**, *E.* See **Milner**, *G.*
**Spooner**, *C. E.* See **Belcher**, *R.*
**Spoor**, *N. L.* See **Anderson**, *J. S.*
**Spring**, *F. S.* See **Baxter**, *R. A.*, and **Ewen**, *E. S.*
**Stack**, *M. V.* See **Petrow**, *V. A.*
**Starling**, *W. W.* See **Petrow**, *V. A.*
**Stead**, *D. M.* See **Peters**, *A. T.*
**Steger**, *L.* See **Cook**, *A. H.*
**Stephenson**, (*Miss*) *E. F. M.* See **Hatt**, *H. H.*
**Stonehill**, *H. I.*, transport numbers of nitric acid in water at 25° from E.M.F., 647.
**Sugden**, *S.*, magnetochemistry, 328.
**Sundralingam**, *A.* See **Farmer**, *E. H.*
**Sutherland**, (*Miss*) *M. M. J.* See **Sharp**, *W.*
**Sutton**, *D. A.* See **Farmer**, *E. H.*

T.

**Tadros**, *W.*, and **Schönberg**, *A.*, preparation of the œstrogen β-bromo-β-phenyl-αα-di(*p*-ethoxyphenyl)ethylene, 394.
**Tárnoky**, *A. L.* See **Balfe**, *M. P.*
**Taylor**, *R.*, obituary notice of, 510.
**Todd**, *A. R.* See **Baddiley**, *J.*, **Bergel**, *F.*, and **Kenner**, *G. W.*
**Topham**, *A.* See **Kenner**, *G. W.*
**Tucker**, *S. H.* See **Preston**, *R. W. G.*
**Turner**, *H. S.* See **Hodgson**, *H. H.*

V.

**Vallance**, *R. H.*, obituary notice of, 44.
**Vogel**, *A. I.*, physical properties and chemical constitution. Part VIII. Alkyl chlorides, bromides, and iodides, 636.

**Vogel**, *A. I.*, and **Cowan**, *D. M.*, physical properties and chemical constitution. Part VII. Alkyl sulphides, disulphides, sulphites, sulphates, and orthophosphates, 16.

**W.**

**Walker**, *N.* See **Burton**, *H.*
**Warren**, *F. L.* See **Richardson**, (*Miss*) *M. F.*
**Watson**, *J.* See **Mann**, *F. G.*
**Way**, (*Miss*) *Y. M.* See **Haworth**, *R. D.*
**Weil-Malherbe**, *H.*, experimental study of chromatography, 303.
**Weiss**, *J.*, theory of chromatography, 297.
formation and structure of organic molecular compounds. Part II. Molecular compounds of *s*-trinitrobenzene with unsaturated ketones, 462.
**White**, *T.*, synthesis of methacrylic acid, 238.
**White**, *T.*, and **Haward**, *R. N.*, preparation and polymerisation of methyl vinyl ketone, 25.
**Williams**, *H. E.*, variation of colour of crystals of commercial sodium and potassium ferrocyanide [cyanoferrate (II)], 223.
**Wilson**, *F. J.* See **Sharp**, *W.*
**Woolfe**, *G.* See **Bergel**, *F.*
**Woolman**, *A. M.* See **Bance**, *S.*, and **Barber**, *H. J.*
**Wragg**, *W. R.* See **Petrow**, *V. A.*
**Wynne**, *W. P.* See **Chatt**, *J.*

**Y.**

**Young**, *W. J.*, obituary notice of, 44.

**Z.**

**Zaki**, *A.*, and **Azzam**, *R. C.*, preparation of 3-alkylchromones; effect of substitution on reactivity of the 2-methyl group in chromones, 434.
**Zaki**, *A.*, and **Iskander**, *Y.*, action of phosphorus pentachloride on non-symmetrically substituted acetones, 68.

# INDEX OF SUBJECTS, 1943.


## A.

**Acetaldehyde,** condensation products of, 42.
**Acetaldol,** polymerisation of, 445.
**Acetanilide,** 2:3:5:6-*tetra*chloro-*N*-nitro-, 372.
**Acetic acid,** 4-bromo-, 4-chloro-, and 4-iodo-naphthyl esters, 469.
**Acetic acid,** chloro-, sodium salt, elimination of chlorine from, 517.
cyano-, dissociation constant of, 516.
halogeno-, derivatives, salts, hydrolysis of, Brönsted catalysis relation in, 521.
**Acetoacetic acid,** ethyl ester, diphenylenehydrazone, 660.
**Aceto-1-naphthalide,** 4-bromo-, nitration of, 321.
2:4-*di*chloro-6-nitro-, 392.
*N*-nitroso-, 285.
**Aceto-2-naphthalide,** 3-nitro-, 636.
**Acetone** diphenylenehydrazone, 660.
reaction of, with benzhydrol in sunlight, 276.
*as*-substituted derivatives, action on, of phosphorus pentachloride, 68.
***N*-Acetonylglycine,** *N*-benzenesulphonyl derivative, and its 2:4-dinitrophenylhydrazone, 377.
**Acetophenone,** *p*-chloro-, phenylhydrazone, 67.
**Aceto-*m*-toluidide-6-sulphonamide,** and bromo-, 78.
**Aceto-*m*-toluidide-6-sulphonanilamide,** 78.
**2-Acetyldiphenylamine,** 4-nitro-3′- and -4′-amino-, acetyl derivatives, 346.
**Acetylmandelamidoethanesulphonic acid,** sodium salt, 5.
**Acetyl-*r*-mandelic acid,** solubility of, in water, 231.
**2-Acetyl-4′-methyldiphenylamine,** 4-nitro-, 347.
**α-Acetyltetronic acid,** 242.
**Acetylursolic acid,** oxidation of, 523.
**Acids,** *mono*basic, dissociation constants of, 511, 513.
dissociation constants of, in mixed solvents, 270.
long-chain, containing quaternary carbon atoms, 615.
reactions of, and their derivatives, in Friedel–Crafts synthesis, 425.
**Acridine,** derivatives, preparation and therapeutic properties of, 344.
**Acridine,** 5-amino-, acetyl derivative, 457.
3:5-*di*amino-, 4-hydroxy-, and 3-nitro-5-amino-, hydrochloride, 461.
**Acridines,** preparation and therapeutic properties of, 5.
**Acridines,** amino-, antiseptic power and properties of, 454, 458.
nature of amino-group in, 454, 458.
partition coefficients and surface activities of, 651.
**Acridine-7-carboxylic acid,** 2-amino-, 458.
**Acridone-7-carboxylic acid,** 7-nitro-, 458.
**α-Acyltetronic acids,** synthesis of, 241.
**Address,** presidential, 194.
**Adenine,** synthesis of, 386.
**Adrenaline,** oxidation of, 48.
**Alcohols,** catalytic dehydrogenation of, to aldehydes, 282.
**Aldehydes,** formation of, from alcohols, 282.
preparation of, from acids with titanium dioxide as catalyst, 84.
αβ-unsaturated, absorption spectra of, and of their oximes and semicarbazones, 566.
**Alkaloids** from *Senecio*, 452.
**Alkyl** bromides, constitution and physical properties of, 636.
chlorides, constitution and physical properties of, 636.
cyanides, parachors of, 148.
halides, parachors of, 152.
reaction of, with hydroxylic solvents, 255.
iodides, constitution and physical properties of, 636.
sulphates, physical contents of, 23.
sulphides, physical constants of, 16, 22.
*di*sulphides, physical constants of, 16.
**β-Alkylation** by Grignard reagents, 501.
**3-Alkylchromones,** preparation of, 434.
**9-Alkylpurines,** synthesis of, 383, 386.
***N*-Allylglycine,** *N*-benzene- and -toluene-sulphonyl derivatives, 376.
**Aluminium** chloride, action of, on aromatic bromo-compounds, 525.
on phenols, 527.
**Amalgams.** See Mercury alloys.
**Amidines,** reactions of, with malonic acid derivatives, 388.
sulphonyl derivatives of, 101.
**4′-Amidinostilbene,** 2-cyano-, 3.
**Amines,** diazotised, action of cuprous oxide on, 86.
**Amino-acids,** basic anhydrides of, 39.
**Ammonia,** compounds of, with metallic salts, 104.
**8-*n*-Amyl-γ-aminopropylamino-6-methoxyquinoline,** 8-ε-amino-, and its salts, 564.
***n*-Amyloxybenzoic acid,** 432.
**Analysis,** organic, micro-, 313.
qualitative semi-micro-, 72.
**Androstendiones,** stereoisomeric, 491.
***cis*-Δ$^5$-Androstene-3:4-diol-17-one,** 138.
**Δ$^5$-Androsten-3(β)ol-17-one,** 4-hydroxy-, acetyl derivative, 138.
**Anilides,** halogenation of, 430.
**Aniline,** 2:3:5:6-*tetra*chloro-, and 2:3:5:6-*tetra*chloro-4-nitro-, and their derivatives, 233.
2:3:5:6-*tetra*chloro-4-nitro-, amination of, 576.
2:3:5:6-*tetra*chloro-*N*-*mono*- and -*N*:4-*di*-nitro-, 373.
*p*-iodo-, compound of, with *s*-trinitrobenzene, 153.
**Anilinoacridines,** 461.
**4-Anilinoanthraquinone-2-sulphonic acid,** 1-amino-, *p*-toluidine salt, 46.
**1-Anilinoanthraquinone-3-sulphonic acid,** sodium and *p*-toluidine salts, 46.
**1-Anilino-4-*p*-toluidinoanthraquinone,** 47.
**4-Anilino-1-*p*-toluidinoanthraquinone-2-sulphonic acid,** sodium and *p*-toluidine salts, 47.
**2-β-Anilinovinyldihydro-1:3-thiazine** methiodide, and its acetyl derivative, 247.
**1-Anilino-4-*m*-4′-xylidinoanthraquinone,** 47.
**4-Anilino-1-*m*-4′-xylidinoanthraquinone-2-sulphonic acid,** sodium and *p*-toluidine salts, 47.
**Anions,** basic, reactivity of, 517.
***o*-Anisidine,** 3:4:6-*tri*- and 3:4:5:6-*tetra*-chloro-, 3:4:6-*tri*chloro-5-amino-, -5-bromo-, and -5-nitro-, and their derivatives, 236.
***o*-Anisidines,** *poly*halogeno-, and their derivatives, 235.
**Anisole,** 3:4:6-*tri*chloro-2:5-*di*amino-, and its derivatives, and 3:4:6-*tri*chloro-2-nitro-, 236.
2:3:5:6-*tetra*chloro-4-amino-, and -4-nitro-, and their derivatives, 234.
**β-*p*-Anisylbutyrophenone,** γ-nitro-, 593.
**α-*p*-Anisyl-Δ$^α$-propylene,** β-bromo-, and α- and β-chloro-, 611.
**1-*p*-Anisylprop-1-yne,** 611.
**Annual General Meeting,** 170.
**Anthranil,** reaction of, with maleic anhydride, 654.
**Anthranoyl-lycoctonine,** 141.
**Anthraquinone-2-sulphonic acid,** 1:4-*di*amino-, sodium salt, 47.
4-bromo-1-amino-, *p*-toluidine salt, 47.
**Antimalarials,** new, 555, 557, 561.
***d*(—)-Arabinose,** 2:4-*di*nitrophenylhydrazone, 628.
**Aromatic compounds,** halogenation of, 276, 279.
**Aryl** nuclei, union of, 441.
**1-Aryl-3:3-dimethyltriazens,** reactions with, 441.
**Azoimide,** decomposition of, and its reaction with substituted benzoic acids, 421.

## B.

**Bacteria,** growth of, physical chemistry of, 208, 213, 219.
inhibition of, by metabolite analogues, 322.

*Bacterium lactis aerogenes*, growth of, in various media, 208, 213, 219.
rate of, 219.
**Balance sheets**, 176, 182.
**Barium** bromide, ammines and deuterammines of, 118.
**Bases**, aromatic, nuclear alkylation of, 14.
**Benzdioxin**, substituted derivatives, action of alkalis on, 319.
**Benzene**, 1:2:4:5-*tetra*chloro-, derivatives of, 233, 372, 576.
*di*chloro*tri*amino-derivatives, 3:5-*di*chloro-1-nitro-2:6-*di*amino-, and its diacetyl derivative, and 3:5-*di*chloro-1-nitro-2:4:6-*tri*amino-, 576.
2:3:5:6-*tetra*chloro-1:4-*di*amino-, and its derivatives, 234.
2:3:5:6-*tetra*chloronitro-, amination of, 576.
*s-tri*nitro-, compound of, with *p*-iodoaniline, 153.
compounds of, with unsaturated ketones, 462.
**Benzeneazo-2′-hydroxy-3′-naphthanilide**, 2:3:5-*tri*chloro-4-bromo-6-hydroxy- and -4-nitro-6-hydroxy-, 237.
2:3:5:6-*tetra*chloro-4-nitro-, 234.
**1-Benzeneazo-2-naphthol**, 4-bromo-, 4-chloro-, and 4-iodo-, 469.
2:3:5:6-*tetra*chloro-, 2:3:5:6-*tetra*chloro-4-amino-, 2:3:5:6-*tetra*chloro-4-hydroxy-, and 2:3:5:6-*tetra*chloro-4-nitro-, 234.
**Benzeneazophenols**, 3:4-*m*- and 4:2-*p*-*di*nitro-, 380.
**5-Benzeneazopyrimidine**, 4:6-*di*amino-, 387.
**Benzene-2-diazo-1-oxide**, 3:4:6-*tri*chloro-, and 3:4:6-*tri*chloro-5-nitro-, 237.
**Benzene-4-diazo-1-oxide**, 2:3:5:6-*tetra*chloro-, 235.
**Benzenediazosulphonic acids**, isomeric, potassium salts, structure of, 470.
**Benzenesulphonamide**, *p*-hydroxylamino-, complex formation and rearrangement of, 656.
**ε-Benzenesulphonamido-*n*-butyric acid**, γ-amino-α-*p*-amino-, 40.
**ε-Benzenesulphonamido-*n*-hexoic acid**, ε-amino-α-*p*-amino-, 40.
**8-γ-Benzenesulphonamidopropylamino-6-methoxyquinoline**, 8-γ-*p*-amino-, γ-*p*-acetyl derivative, 559.
**Benzenesulphonylacetimino-ether**, 4-nitro-, 103.
***N*-Benzenesulphonyl-*N*-allylalanine**, 378.
***N*-Benzenesulphonyl-*N*-allylaminoacetic acid**, *N*-*m*-nitro-, ethyl ester, 378.
**Benzenesulphonyl-α-aminopropionic acid**, ethyl ester, 378.
***N*-Benzenesulphonylbenzamidine**, 4-amino-, and its acetyl derivative, and 4-nitro-, 103.
**Benzenesulphonylbenzimino-ether**, 4-amino-, and 4-nitro-, and their derivatives, 103.
***N*-Benzenesulphonylglycine**, *N*-*m*-nitro-, and its ethyl ester, 378.
***N*-Benzenesulphonyl-*o*-phenylbenzimino-ether**, *N*-*p*-nitro-, 103.
**Benzhydrol**, reaction of, with acetone in sunlight, 276.
**Benz*cyclo*octatetraenes**, 326.
**Benzoic acid**, dissociation constants of, 271.
**Benzoquinone**, tautomerism of, in systems with *p*-nitrosophenol, 89.
**Benzo-*m*-toluidide-6-sulphonamide**, 79.
**β-Benzoyl-α-(*p*-acetamidophenyl)propionitrile**, 593.
**β-Benzoyl-αα-dimethyl-*n*-butyric acid**, and its methyl ester, 428.
**β-Benzoyl-αα-dimethylpropionic acid**, and its derivatives, 428.
**β-Benzoyl-αβ-dimethylpropionic acid**. See β-Benzoyl-α-methyl-*n*-butyric acid.
**β-Benzoyl-ββ-dimethylpropionic acid**, and its methyl ester, 429.
***O*-Benzoyl-*r*-mandelic acid**, 228.
solubility of, in water, 231.
**α-Benzoyl-α-2-methoxy-4-methylbenzoylacetone**, 435.
**β-Benzoyl-α-methyl-*n*-butyric acid**, and its derivatives, 428.
**Benzoylphenacylamine**, 317.
**β-Benzoyl-ααβ-trimethylpropionic acid**. See β-Benzoyl-αα-dimethyl-*n*-butyric acid.
**Benzpinacol**, formation of, from benzhydrol, 276.
**Benzpyrene**, determination of, 312.
**Benzyl alcohol**, dehydrogenation of, 284.
**Benzyl alcohol**, *o*-hydroxy-, 475.
**8-γ-Benzylaminopropylamino-6-methoxyquinoline**, and its salts, 563.
**α-Benzyl-$\Delta^{\alpha}$-butylene**, α-chloro-, 69.
**3-Benzyl-2:7-dimethylchromone**, 435.
**α-Benzylethylene**, α-chloro-α-*p*-nitro-, 70.
**Benzylideneaminoacridines**, 460.
**Benzylidene-*p*-anisylideneacetone**, compounds of, with *s*-trinitrobenzene, 463.
**5-Benzyl-12-methyl-1:2:3:4:12:13-hexahydroxanthen**, 5-*o*-hydroxy-, 476.
***m*-Benzyloxybenzoic acid**, and *p*′-bromo-, *p*′-chloro-, and *p*′-fluoro-, 432.
**α-Benzyl-$\Delta^{\alpha}$-propylene**, α-chloro-, 69.
**Benzylsuccinic acid**, 3-chloro-, and its anhydride, 12.
**3:7-Bis(acetamido)-5-*p*-acetamidostyrylacridine**, 347.
**Bis-(4:4′-acetoxycholesteryl) sulphite**, 139.
**8-Bis-γ-aminopropylamino-6-methoxyquinoline** *tri*hydrochloride, 556.
**Bis-(8-γ-chloropropylamino-6-methoxy-5-quinolyl) sulphide**, and its hydrochloride, 562.
**Bis-(8-γ-diethylaminopropylamino-6-methoxy-5-quinolyl) sulphide**, and its hydrochloride, 562.
**Bis-2-(3-ethyldihydro-1:3-thiazine)trimethincyanine iodide**, 249.
**Bis-2-(3-ethyl*peri*naphtha-1:3-thiazine)trimethincyanine iodide**, 489.
**3:3′-Bishydroxymethylbenzophenone**, 5:5′-*di*nitro-2:2′-*di*hydroxy-, and its phenylhydrazone, 321.
**[(Bis-2-(3-hydroxy-1-methylquinoxaline)]trimethincyanine acetate**, 396.
**γδ-Bis-4-hydroxyphenylhexane-γδ-diol**, and its derivatives, 611.
**γγ-Bis-4-hydroxyphenylhexan-δ-one**, and its dibenzoate, 612.
**[2-Bis-(3-keto-1:4-dimethyldihydroquinoxaline)]trimethincyanine sulphate**, 396.
**Bis-3-(2-keto-1-methyl-1:2-dihydroquinoxalinyl)methane**, 400.
**[Bis-2-(3-keto-4-phenyl-1-methyldihydroquinoxaline)]trimethincyanine sulphate**, 397.
**Bis-2-(3-methyldihydro-1:3-thiazine)trimethincyanine iodide**, 249.
**Bis-2-(3-methyl*peri*naphtha-1:3-thiazine)pentamethincyanine iodide**, 489.
**Bis-2-(3-methyl*peri*naphtha-1:3-thiazine)trimethincyanine iodide and methyl sulphate**, 489.
***s*-Bis-α-4-pyridylphenylurea**, 413.
**(αβ-Bis-*p*-tolylethylamino)vinylbenzene**, *p*-chloro-, 67.
**Biuret**, properties of, 603.
**Boron** hydrides, structure of, 250.
**Brass**, determination in, of lead, volumetrically, 41.
**Bromination**, aromatic, kinetics of, 276.
**Butaldehyde**, condensation of, with 3-methylpent-2-en-4-yne, 265.
***n*-Butoxybenzoic acid**, 432.
**Butyl alcohol**, dehydration of, 283.
***n*-Butyl** bromide, reaction of, with hydroxylic solvents, 255.
***iso*Butylaminoacetic acid**, *N*-β-chloro-, ethyl ester, *N*-*p*-toluenesulphonyl derivative, 377.
**5-Butylaminoacridine** hydrochloride, 654.
**8-*n*-Butyl-γ-aminopropylamino-6-methoxyquinoline**, 8-δ′-amino-, and its salts, 564.
**8-γ-Butylaminopropylamino-6-methoxyquinolines**, and their salts, 563.
**β-(*p*-*tert*.-Butylbenzoyl)propionic acid**, semicarbazone, 145.
***N*-*iso*Butylglycine**, *N*-β-hydroxy-, 378.
**β-*tert*.-Butylnaphthalene**, 144.
**Butylnaphthalenes**, and their derivatives, 144.
**2-*tert*.-Butyl-1:4-naphthaquinone**, and its derivatives, 145.
**γ-(*p*-*tert*.-Butylphenyl)butyramide**, 145.
**4-*tert*.-Butylphthalic acid**, and its anhydride, 145.
**4-*tert*.-Butylpyridylbenzene**, 2- and 3-amino-, and 2- and 3-nitro-, and their picrates, 412.
***n*-Butyric acid**, γ-cyano-, preparation of, and its dissociation constant, 516.
*dl-erythro*-αβ-*di*hydroxy-, esters, 467.
**Bromo-compounds**, aromatic, action of aluminium chloride on, 525.

C.

**Calcium** halides, ammines and deuterammines of, 118.
*Cannabis indica*, 286.
**Carbazole**, 9-amino-, picrate, 660.
**2-*o*-Carboxybenzoyl-1:2:3:4-tetrahydrophthalazine**, and its sodium salt, 658.
**3-*O*-Carbethoxy-6-acetoxy-$\Delta^{4}$-cholesten-3-ol**, 440.
**3-*O*-Carbethoxy-4-acetoxycholesterol**, 440.

**3-*O*-Carbethoxy-4-benzoyloxycholesterol**, 440.
**2-β-Carbethoxyethyl-Δ¹-*cyclo*hexene-1-cyanoacetic acid**, ethyl ester, 502.
**3-*O*-Carbethoxy-4-hydroxycholesterol**, 440.
**2-Carbethoxy-3-(2′-keto-1′-methyldihydro-3′-quinoxalyl)indole**, 400.
**2-Carbethoxy-3-(3′-methyl-2′-quinoxalyl)indole**, 400.
**Carbocyanines** containing *peri*naphtha-1:3-thiazine nucleus, 487.
**3-*O*-Carbomethoxy-4-acetoxycholesterol**, 439.
**3-*O*-Carbomethoxy-4-benzoyloxycholesterol**, 439.
**3-*O*-Carbomethoxy-4-hydroxycholesterol**, 439.
**2-Carbomethoxy-6-hydroxy-2:5-dimethyldecalin-2-acetic acid**, methyl ester, 496.
**α-2-Carbomethoxy-6-hydroxy-2:5-dimethyltetralin-1-acetic acid**, 496.
**α-2-Carbomethoxy-6-methoxy-2:5-dimethyltetralin-1-β-propionic acid**, methyl ester, 496.
**1-*o*-Carbomethoxyphenyl-3:3-dimethyltriazen**, 443.
**Carbonyl compounds**, spectra of, absorption, and of their derivatives, 565.
**8-ω-Carboxydecylamino-6-methoxyquinoline**, and its derivatives, 559.
**2-Carboxy-4:6-dimethoxynaphthalene-1-acetic acid**, 501.
**α-2-Carboxy-6-hydroxy-2:5-dimethyltetralin-1-acetic acid**, methyl ester, 496.
**2-Carboxy-6-methoxy-2:5-dimethyltetralin-1-acetic acids**, and their derivatives, 494.
**1-Carboxymethylene-6-methoxy-2:5-dimethyltetralin-2-carboxylic acid**, derivatives of, 494.
**1-*o*-Carboxyphenyl-3:3-dimethyltriazen**, 443.
**Carrageheen moss**, polysaccharides of, 51.
**Catalysis**, Brönsted relation in, of hydrolysis of halogenoacetates, 521.
**Catalysts**, titanium *di*oxide, 84.
**Catalytic** reduction by formic acid with copper or nickel, 281.
*Cetraria islandica*. See Iceland moss.
**Chlorination**, aromatic, kinetics of, 279.
**Cholestane**, 5-chloro-3:6-*di*hydroxy-, 3-acetyl-6-benzoyl derivative, 614.
**Δ⁵-Cholestene**, 4-chloro-3-hydroxy- and 3:4-*di*hydroxy-, derivatives of, 138.
***cis*-Δ⁵-Cholestene-3:4-diol**, esters, acyl migrations in, 437.
**Δ⁵-Cholesten-3-ol**, 4-hydroxy-, derivatives of, 137.
**Δ⁵-Cholesten-4-ol**, 3-hydroxy-, derivatives of, 138.
**Δ⁴-Cholestenone**, 602.
**β-Cholesterol** oxide, and its derivatives, 613.
*Chondrus crispus*. See Carrageheen moss.
**Chromatography**, 297, 303.
**Cinnolines**, 447.
**Citral**, condensation of, with 3-methylpent-2-en-4-yne, 265.
**Coal**, carbonisation product of, 578.
**Cobalt bases**, interchange of hydrogen in, with deuterium oxide, 361.
**Coke**, properties of, 578.
**Compounds**, molecular, structure of, 153, 435.
**Constitution**, molecular volume and, 146.
physical properties and, 16, 636.
**Copper**, catalytic reduction by formic acid with, 281.
**Cuprous** oxide, action of, on diazotised amines, 86.
sulphate, ammines and deuterammines of, 118.
**Copper organic compounds** : —
**Cuprous** cyanide, 79.
***p*-Cresol**, 2:5- and 2:6-*di*bromo-, and 3-chloro-2:5-*di*bromo-, 526, 527.
**Cresols**, nitrosation of, and their methyl ethers, 221.
***m*-Cresol-6-sulphonamide**, 79.
**Crotonaldehyde**, acetylenic glycol from, and its rearrangement, 268.
condensation of, with 1-hexyne, 264.
with 3-methylpent-2-en-4-yne, 265.
oxygen absorption by, in presence of catalysts, 463.
**Crotonic acid**, crotyl ester, 467.
**Crotyl-3:5-*di*nitrophenylurethane**, 467.
**Cyanines**, quinoxaline, 394, 397.
**Cyano-acids**, dissociation constants of, 513.
**Cyanoferrates**. See Hydroferrocyanic acid, salts.
**Cyanogen** : —
**Hydrocyanic acid**, cuprous salt, 79.

D.

**Deca-2:8-dien-5-yn-4:7-diol**, 269.
**Deca-3:7-dien-5-yn-2:9-diol**, and its derivatives, 269.
**Decane-2:9-diol**, and its derivatives, 269.
**Decane-2:9-dione**, and its dioxime, 269.
**Dec-2-en-5-yn-4-ol**, and its derivatives, 264, 265.
**Dec-3-en-5-yn-2-ol**, and its derivatives, 265.
**8-Decyl-ω-aminodecylamino-6-methoxyquinoline**, 8-ω-amino-, and its meconate, 558.
**8-Decylamino-6-methoxyquinoline**, 8-ω-amino-, *di*hydrochloride, 558.
8-ω-cyano-, 560.
**8-Decyl-γ-aminopropylamino-6-methoxyquinoline**, 8-ω-amino-, and its meconate, 559.
**8-Decylaminoquinoline**, 8-ω-cyano-, 560.
**β-*n*-Decyl-β-*n*-dodecylpropionic acid**, 618.
**1-*n*-Decyl*cyclo*hexane-1-cyanoacetic acid**, ethyl ester, 502.
**3-Decyltridecanol**, 619.
**3-Decyl-Δ²-tridecenoic acid**, ethyl ester, 619.
**3-Decyltridecoic acid**, ethyl ester, 619.
**3-Decyltridecylmalonic acid**, ethyl ester, 619.
**Delatine**, and its hydrochloride, 140.
**Delpheline**, and its salts, 140.
*Delphinium elatum*, alkaloids of, 139.
**2:2-Dialkyl*cyclo*hexanones**, derivatives, preparation of, 661.
***trans*-4:4′-Diamidino-αβ-dimethylstilbene**, *di*hydrochloride, 101.
**4:4′-Diamidino-βγ-diphenylbutane**, and its dihydrochloride, 101.
***cis*-4:4′-Diamidinostilbene**, 4.
**4:4′-Diamidinotolane**, *di*hydrochloride, 3.
**1:4-Dianilinoanthraquinone-2-sulphonic acid**, sodium and *p*-toluidine salts, 46.
**αδ-Di-*p*-anisyl-βγ-dimethyl-Δ^αγ-butadiene**, 611.
**αδ-Di-*p*-anisyl-βγ-dimethylbutane**, 611.
**2:2′-Di-*p*-anisyl-4:4′-diphenylazadipyrromethine**, 593.
**γδ-Di-*p*-anisylhexane-γδ-diol**, 611.
**Dianisylideneacetone**, compounds of, with *s*-trinitrobenzene, 463.
**3:3′-(Di-*p*-anisylideneamino)-2:2′:4:4′-tetraphenyl-*meso*-*p*-anisyldipyrromethine**, 598.
**2:3-Di-*p*-anisylquinoxaline**, 612.
**1:1′-Dianthraquinonyl**, 4:4′-*di*amino-, and 2:2′-*di*bromo-4:4′-*di*amino-, 47.
**2:2′-Dianthraquinonyl-1:1′-dicarboxylic acid**, and *di*nitro-, and their esters, 32.
**1:1′-Dianthraquinonyl-3:3′-disulphonic acid**, 4:4′-*di*amino-, sodium and *p*-toluidine salts, 47.
**2:4-Diarylpyrroles**, 590, 596, 598.
**7:16-Diazanaphthacene**, derivatives of, 658.
***p*-Diazine** *di*-*N*-oxides, 324.
**1-Diazoanthraquinone-2-sulphonic acid**, salts, action of bases on, 45.
**Diazo-compounds**, decomposition of, in neutral solution, 379.
**Diazonaphthols**, preparation of, 321.
resonance structure of, 468.
**1-Diazophenylaminoanthraquinone-2-sulphonic acid**, aniline salt, 46.
**Dibenzanthrone**, *di*nitro-, 31.
**αα′-Di(benzenesulphonamido)*iso*propyl alcohol**, *di*-*p*-amino-, and its diacetyl derivative, 608.
**Dibenzenesulphonanilide**, *di*-4-nitro-, 103.
**Dibenzoylphenacylamine**, 317.
**Dibenzylideneacetone**, compounds of, with *s*-trinitrobenzene, 463.
**3:3′-Dibenzylideneamino-2:2′:4:4′-tetraphenyl-*meso*-phenyldipyrromethine**, 598.
**Dicinnamylideneacetone**, compounds of, with *s*-trinitrobenzene, 463.
**Dienœstrol**, and its derivatives, 609.
**4:4′-Diethoxydiphenylamine**, 65.
**Di-(*p*-ethoxyphenyl)benzylcarbinol**, 394.
**2:4-Diethylacetophenone**, 6-hydroxy-, *di*bromo-derivative, 274.
**3:4-Diethylacetophenone**, 6-hydroxy-, bromo-derivative, 274.
**8-β-Diethylaminoethylamino-6-methoxyquinoline**, 5-chloro-, 556.
**8-γ-Diethylaminopropylamino-6-methoxyquinoline**, and its salts, 564.
**8-ω-Diethylaminoundecylamino-6-methoxyquinoline**, 5-chloro-, hydrochloride, 559.

*NN'*-**Diethylethylenediamine**, *NN'-di*-β-amino-, preparation of, 609.
**2:6-Di-α-furylpyrimidine**, 4-amino-5-cyano-, 390.
**Dihydromyrcene**, 476.
**Dihydromyrcene**, *mono-* and *di*-chloro-, 296.
α- and β-**Dihydrotutin**, 143.
**2':3'-Diketo-4:6-dimethoxy-1:2-*cyclo*pentenonaphthalene**, 501.
**3':6-Diketo-2:5-dimethyldecahydro-1:2-*cyclo*pentenonaphthalene-x-α**, 497.
**2':3'-Diketo-4-methoxy-1:2-*cyclo*pentenonaphthalene**, 499.
**4:7-Diketo-*m*-methoxyphenylheptoic acid**, 499.
**6:17-Diketo-6:8:15:17-tetrahydro-7:16-diazanaphthacene**, and 1-amino-, and its benzoyl derivative, and 1-nitro-, 658.
**4:6-Dimethoxy-5:6:7:8-tetrahydro-1:2-*cyclo*pentenonaphthalene-3'-acetic acid**, 499.
**Dimethyl** ether. See Methyl ether.
**5:7-Dimethylacridine**, 3-amino-, and its derivatives, and 3-nitro-, 347.
**αγ-Dimethylallyl alcohols**, optically-active, 348.
**αγ-Dimethylallyl** chloride, preparation and reactions of, 349.
phenylurethane, 351.
**5-Dimethylaminoacridine** hydrochloride, 461.
**β-(*p*-Dimethylaminophenyl)butyrophenone**, γ-nitro-, and its oxime, 593.
**5-*p*-Dimethylaminostyrylacridine** methochloride, 7.
**ψ-2-*p*-Dimethylaminostyryl-1-γ-aminopropylquinolinium** bromide hydrobromide, 6-amino-, 560.
**2-*p*-Dimethylaminostyryl*peri*naphtha-1:3-thiazine**, and its derivatives, 491.
**ψ-2-*p*-Dimethylaminostyryl-1-γ-phthalimidopropylquinolinium** bromide, 6-amino-, acetyl derivative, 560.
**Dimethylbutylcarbinol** phenylurethane, 263.
**α-(2:2-Dimethylchromanyl-3)-β-(2:3-dimethylchromanyl-2)-ethane**, 476.
**2:7-Dimethylchromone**, 434.
**Dimethylcyanoacetic acid**, preparation of, and its dissociation constant, 516.
**2:5-Dimethyldecahydro*cyclo*pentenonaphthalene**, 3':6-*di*hydroxy-, 497.
**2:4-Dimethyl-*N*-ethylaniline**, 65.
**2:7-Dimethyl-3-ethylchromone**, 434.
**7:12-Dimethyl-1:2:3:4:12:13-hexahydroxanthen**, 476.
**1:2-Dimethyl-3-(γ-methyl-$\Delta^{\gamma}$-pentenyl)chroman**, 476.
**3:6-Dimethyl-2-morpholone**, *N*-benzenesulphonyl derivative, 378.
**6:6-Dimethyl-2-morpholone**, *N*-benzene- and -toluene-sulphonyl derivatives, 377.
**2:4-Dimethyl-1-naphthol**, and its picrate, 168.
**3:5-Dimethylphenyl** ethers, 4-chloro-, and 4-chloro-2-nitro-, 445.
**2:7-Dimethyl-3-*n*-propylchromone**, 434.
**6:9-Dimethylpurine**, 2-hydroxy-, 385.
**2':6'-Dimethylpyridylquinolines**, 416.
**2:6-Dimethylpyrimidine**, 4-amino-5-cyano-, 389.
**2:3-Dimethylquinoxaline**, Diels–Alder synthesis with, 654.
**αβ-Dimethylstilbene**, 4:4'-*di*bromo- and *-di*cyano-, 100.
**1:3-Dioxanyl-5-*iso*butenyl ketone**, 30.
**αγ-Diphenylacetoacetic acid**, α-2:4-*di*nitro-, ethyl ester, 69.
**Diphenylalkanes**, bromination of, 1, 99.
**Diphenylamine-2'-aldehyde**, 2-nitro-, 460.
**Diphenylamine-2:4'-dicarboxylic acid**, 5-nitro-, 458.
**Di-(β-phenylamino-α-*p*-chlorophenylvinyl)** ether, and its diacetyl derivative, 65.
*NN*-**Di-(β-phenylamino-α-*p*-chlorophenylvinyl)aniline**, 66.
*NN*-**Di-(β-phenylamino-α-phenylvinyl)aniline**, 64.
*NN'*-**Diphenylbenzamidine**, *p*-nitrobenzenesulphonate, 103.
**βγ-Diphenyl-*n*-butane**, bromination of, 99.
**βγ-Diphenyl-*n*-butane**, *di-*, *tri-*, and *tetra*-bromo-, and *di*cyano-derivatives, 100.
**3:4-Diphenylcinnoline**, 450.
**2:2'-Diphenyl-4:4'-di-(*p*-acetamidophenyl)azadipyrromethine**, 593.
**2:2'-Diphenyl-4:4'-di-*p*-anisylazadipyrromethine**, 593.
**2:2'-Diphenyl-4:4'-di-(*p*-dimethylaminophenyl)azadipyrromethine**, and its dimethiodide, 593.
**2:2'-Diphenyl-4:4'-di-(*m*-hydroxyphenyl)azadipyrromethine**, 593.
**2:2'-Diphenyl-4:4'-di-(3:4-methylenedioxyphenyl)azadipyrromethine**, 593.
**2:2'-Diphenyl-4:4'-di-(*m*-nitrophenyl)azadipyrromethine**, 592.
**Diphenylene**, 326.
**αβ-Diphenylethane**, bromination of, 1.
**αβ-Diphenylethane**, *di-* and *tetra*-bromo-derivatives, and αβ-dibromo-4:4'-*di*cyano-, 2.
**2:3-Diphenyl-6-α-pyridylquinoxaline**, 405.
**2:6-Diphenylpyrimidine**, 4-amino-5-cyano-, 390.
**2:4-Diphenylpyrrole**, 3-amino-, and its benzoyl derivative, 598. 5-amino-, and its acetyl derivative, and 5-nitroso-, and its salts, 594.
**2:4-Diphenylpyrrole-5-aldehyde**, and its derivatives, 597.
**2:4-Diphenylpyrrole-5-carbinol**, 597.
**8-Di-γ-phthalimidopropylamino-6-methoxyquinoline**, and its hydrobromide, 556.
***p*-Dipyridylbenzene**, 406.
**1:3-Dipyridylbenzene**, 4-nitro-, 406.
**Dipyridylquinolines**, 404.
**6:8-Dipyridylquinolines**, 406.
**Dissociation constants**, of acids in mixed solvents, 270.
of monobasic acids, 511, 513.
**Di-*p*-toluenesulphon-1-naphthalide**, 6-nitro-, 391.
*NN'*-**Ditoluene-*p*-sulphonyl-1:4-naphthylenediamine**, 636.
*NN*-**Di-(β-*p*-tolylamino-α-phenylvinyl)-*p*-toluidine**, 64.
**Docosahexaenoic acid**, methyl ester, autoxidation of, 124, 546.
**Dodecyl alcohol**, dehydrogenation of, 284.
**5-Dodecylaminoacridine**, hydrochloride, 654.
***n*-Dodecyloxybenzoic acid**, 432.

## E.

**Earths**, rare, metals, alloys of, with mercury, 8, 531.
detection of, in scheelite, 577.
yttrium group, oxalates of, 40.
**Elaidic acid**, oxidation of, and of its methyl ester by hydrogen peroxide in acetic acid, 37.
**Electrolytic oxidation**, studies in, 90.
**Electronic mobility**, effect of substitution on, 380.
**1-Ethoxy-2-2':4'-*di*nitrophenylnaphthalene**, 3-hydroxy-, and its acetyl derivative, 69.
**β-Ethoxy-α-*p*-nitrophenyl-$\Delta^{\alpha}$-propylene**, 70.
**3-Ethoxytoluene-6-sulphonic acid**, and 2- and 4-*mono-* and 2:4-*di*-nitro-, and their derivatives, 168.
**4-Ethoxy-*m*-toluic acid**, and 5-nitro-, 320.
**Ethyl** chloride, heat of adsorption of, on sugar charcoal, 351.
hydrogen sulphate, β-amino-, 4.
**8-γ-Ethylaminopropylamino-6-methoxyquinoline**, and its salts, 562.
**8-Ethyl-γ-aminopropylamino-6-methoxyquinoline**, 8-β'-amino-, and its salts, 563.
8-β-hydroxy-, and its salts, 564.
**Ethylaniline**, 2:4-*di*nitro-β-amino-, and its hydrochloride, 556.
*N*-**Ethylaniline**, *p*-chloro-, and its *p*-toluenesulphonyl derivative, 65.
**[2-(3-Ethylbenzoxazole)][2-(3-ethyl*peri*naphtha-1:3-thiazine)] trimethincyanine** iodide, 491.
**[2-(3-Ethylbenzoxazole)][2-(3-methyl*peri*naphtha-1:3-thiazine)] trimethincyanine** iodide, 490.
***o*-Ethylbenzyl** bromide, *o*-β-bromo-, syntheses with, 547, 550.
**Ethyl-*n*-decyl-*n*-dodecylacetic acid**, and its amide, 618.
**[2-(3-Ethyldihydro-1:3-thiazine)][2-(5-chloro-3-ethylbenzthiazole)]methincyanine** iodide, 248.
**[2-(3-Ethyldihydro-1:3-thiazine)][2-(3-ethyl-4:5-benzbenzthiazole)]methincyanine** iodide, 247.
**[2-(3-Ethyldihydro-1:3-thiazine)][2-(3-ethyl-6:7-benzbenzthiazole)]methincyanine** iodide, 247.
**[2-(3-Ethyldihydro-1:3-thiazine)][2-(3-ethylbenzoxazole)]-methincyanine** iodide, 247.
**[2-(3-Ethyldihydro-1:3-thiazine)][2-(3-ethylbenzselenazole)]-methincyanine** iodide, 248.
**[2-(3-Ethyldihydro-1:3-thiazine)][2-(3-ethylbenzthiazole)]-methincyanine** iodide, 247.
**[2-(3-Ethyldihydro-1:3-thiazine)][2-(1-ethylquinoline)]methincyanine** iodide, 248.
**[2-(3-Ethyldihydro-1:3-thiazine)][4-(1-ethylquinoline)]methincyanine** iodide, 248.
**8-Ethylmethyl-γ-aminopropylamino-6-methoxyquinoline**, 8-β-hydroxy-, and its salts, 565.
**5-Ethyloct-5-en-7-yn-4-ol**, and its α-naphthylurethane, 263.
**4-Ethylphenol**, bromo-, and *di*bromo-, and their *p*-nitrobenzoates, 526.

**[2-(1-Ethylquinoxaline)][2-(1-ethylbenzthiazole)]trimethincyanine** iodide, 2-3-hydroxy-, 396.
**5:2′-(3′-Ethyltetrahydro-1′:3′-thiazyl)-3-ethylrhodanine,** 249.
**2-Ethylthiodihydro-1:3-thiazine,** and its derivatives, 246.
*N*-**Ethyl-***p*-**toluidine,** and its *p*-toluenesulphonyl derivative, 65.
**Ethynylcarbinols,** isomerisation of, 261.
**Europium,** determination of, in samarium, 533.
isolation of, 531.

F.

**Ferrous** chloride. See under Iron.
**Fish oils,** acids of, and their esters, autoxidation of, 122.
**Formaldehyde,** electrolytic oxidation of, 90.
**Formic acid,** catalytic reduction by, under pressure, 84, 281.
**Formo-1-naphthalide,** 6-nitro-, 391.
**Friedel–Crafts reaction,** reactions of acid derivatives, effect of alkylation on, 425.
**Fries rearrangement,** 79, 273.
**8-γ-Furfurylaminopropylamino-6-methoxyquinoline,** and its salts, 563.
**Furfurylidene-6-chloro-4-methoxy-3-methylacetophenone,** 500.
**Furfurylidene-3-methoxyacetophenone,** and its 2:4-dinitrophenylhydrazone, 499.
α-(β-**2-Furylacrylyl)tetronic acid,** 242.
β-(α-**Furyl)-β-aminomethylenemalononitrile,** 390.
**7-α-Furylpyrimidine,** 4:6-*di*hydroxy-, 389.

G.

**Gabriel's blue,** constitution of, 598.
**Gallium,** 74, 76.
separation of, from germanite by electrolysis, 74.
**Gallium** perchlorate, and its compounds, 76.
**Germanium,** separation of, from germanite by electrolysis, 74.
**4-Glycosidaminopyrimidines,** 571.
**Grignard reagents,** β-alkylation of cationoid systems by, 501.
**8-ω-Guanyldecylamino-6-methoxyquinoline,** 560.
**8-ω-Guanyldecylaminoquinoline,** and its hydrochloride, 560.
**8-γ-Guanylpropylaminoquinoline,** and its hydrochloride, 560.

H.

**Halogenation,** aromatic, kinetics of, 276, 279.
**Hederagenin,** identity of, with melanthigenin, 70.
**Hemicelluloses** of Iceland moss, 54.
**5-Heptylaminoacridine,** hydrochloride, 654.
**8-γ-*n*-Heptylaminopropylamino-6-methoxyquinoline,** and its salts, 563.
*n*-**Heptyloxybenzoic acid,** 432.
*n*-**Heptyl-***n*-**tetradecylacetic acid,** 618.
**Heterocyclic compounds,** containing nitrogen, 658.
synthesis of, 316.
**5-Hexadecylaminoacridine** hydrochloride, 654.
*trans*-**Hexahydrophthaloyl** chloride, 517.
**Hexamethylbenzene,** molecular compounds of, with picryl chloride, 435.
*cyclo***Hexane,** 1:2-*di*cyano-, 517.
*cyclo***Hexane-2-carboxylic acid,** 1-chloro-1-cyano-, ethyl ester, 517.
*trans-cyclo***Hexane-2-carboxylic acid,** 1-cyano-, 517.
*cyclo***Hexanone-2-carboxylic acid,** ethyl ester, cyanohydrin, 516.
**Hexaureagallium** perchlorate, 77.
*cyclo***Hexene-2-carboxylic acid,** 1-cyano-, ethyl ester, 516.
**Hex-3-en-5-yn-2-ol,** and its derivatives, 263.
*n*- and *iso*-**Hexœstrols,** interconversion of, 232.
**5-*cyclo*Hexylaminoacridine** hydrochloride, 654.
**8-γ-*cyclo*Hexylaminopropylamino-6-methoxyquinoline,** and its hydrogen oxalate, 563.
*cyclo***Hexylcyanoacetic acid,** preparation of, and its dissociation constant, 516.
*n*-**Hexyloxybenzoic acid,** 432.
**1-Hexyne,** condensation of, with crotonaldehyde, 264.
*dl*-**Homopiperidone,** *dl*-3-amino-, and its derivatives, 39.
**Hydrazoic acid.** See Azoimide.
**Hydrocarbons,** aromatic, chlorination of, 279.
**Hydrocyanic acid.** See under Cyanogen.
**Hydroferrocyanic acid,** potassium and sodium salts, colour variation in, 223.
**Hydrogen** isotopes, exchange of, with complex salts, 361, 367.
**Hydropicrotoxinin,** bromo-, 51.
structure of, 143.
**Hydrotutin,** bromo-, structure of, 143.
**Hydroxyalkylamino-acids,** 373.

I.

**Iceland moss,** polysaccharides of, 54.
**Imino-ethers,** sulphonyl derivatives of, 101.
**Indene,** derivatives, 71.
**Indium,** vapour pressure of, 141.
**Indole,** 5-hydroxy-, 49.
**Indoles,** formation of, from phenacylarylamines, 58.
**Indole-2-carboxylic acid,** 5-hydroxy-, and its 5-benzyl derivative, and their methyl esters, 49.
**Iodinin,** structure of, 322.
**Iron : —**
**Ferrous** chloride, ammines and deuterammines of, 118.

K.

**3′-Keto-4-acetoxy-5-methoxy-1:2-*cyclo*pentenonaphthalene,** 499.
**3′-Keto-4-acetoxy-1:2-*cyclo*pentenonaphthalene,** and its derivtives, 498.
**Ketoacetylursolic acid,** and its ethyl ester, 524.
**2-Keto-3-benzyl-1:2-dihydroquinoxaline,** 397.
**3-Ketobutanol,** 29.
**1-Keto-7-*tert*.-butyl-1:2:3:4-tetrahydronaphthalene,** and its semicarbazone, 145.
**2-Keto-9:10-dimethyldecalin,** and its semicarbazone, 502.
**2-Keto-1:3-dimethyl-1:2-dihydroquinoxaline,** 396.
**[2-(3-Keto-1:4-dimethyldihydroquinoxaline)][(4-dimethylaminophenyl)]dimethincyanine,** and its methosulphate, 396.
**[2-(3-Keto-1:4-dimethyldihydroquinoxaline)][2-(1:3:3-trimethylindoline)]trimethincyanine** chloride, 396.
**3′-Keto-6-hydroxy-2:5-dimethyl-1:2:3:4-tetrahydro-1:2-*cyclo*pentenonaphthalene-α,** 496.
**3′-Keto-6-methoxy-2:5-dimethyl-1:2:3:4-tetrahydro-1:2-*cyclo*pentenonaphthalene-2′-carboxylic acid,** methyl ester, 496.
**4-Keto-6-methoxy-1:2:3:4-tetrahydro-2-naphthoic acid,** and 3-bromo-, 12.
*cis*-**2-Keto-9-methyldecalin,** and its derivatives, 502.
**[2-(3-Keto-1-methyl-3:4-dihydroquinoxaline)][2-(1-methylquinoline)]trimethincyanine** iodide, 396.
**2-Keto-1-methyl-1:2-dihydroquinoxaline-3-pyruvic acid,** and its ethyl ester, and its derivatives, 400.
**[2-(3-Keto-1-methyl-3:4-dihydroquinoxaline)][2-(1:3:3-trimethylindoline)]trimethincyanine** iodide, 396.
**3-(2-Keto-1-methyldihydroquinoxalinyl)-3-(2-ketodihydroquinoxalinyl)methane,** 400.
**3-(2-Keto-1-methyldihydroquinoxalyl)-3-(2-ketodihydroquinoxalyl)methane** hydrochloride, 401.
**3-(2-Keto-1-methyldihydroquinoxalyl)-3-(2-keto-1-phenyldihydroquinoxalyl)methane,** and its hydrochloride, 400.
**[2-(3-Keto-4-methyl-1-ethyldihydroquinoxaline)][2-(1-ethylbenzthiazole)]trimethincyanine** iodide, 397.
**4-Keto-6-methyl-1:2:3:4-tetrahydro-2-naphthoic acid,** and 3-bromo-, 12.
**Ketones,** condensation of, with phenols, 486.
unsaturated, compounds of, with *s*-trinitrobenzene, 462.
αβ-unsaturated, absorption spectra of, and of their oximes and semicarbazones, 567.
**2-Keto-1-phenyl-3-benzyl-1:2-dihydroquinoxaline,** 397.
**2-Keto-1-phenyldihydroquinoxaline-3-pyruvic acid,** and its ethyl ester, 400.
**3-(2-Keto-1-phenyldihydroquinoxalyl)-3-(2-ketodihydroquinoxalyl)methane,** 400.
**2-Keto-1-phenyl-3-methyl-1:2-dihydroquinoxaline,** 397.
**[2-(3-Keto-4-phenyl-1-methyldihydroquinoxaline)][(4-dimethylaminophenyl)]dimethincyanine,** and its chloride, 397.
**[2-(3-Keto-4-phenyl-1-methyl-3:4-dihydroquinoxaline)][2-(1-methylbenzthiazole)]trimethincyanine** chloride, 397.
**[2-(3-Keto-4-phenyl-1-methyl-3:4-dihydroquinoxaline)][2-(1-methylquinoline)]trimethincyanine** sulphate, 397.
**[2-(3-Keto-4-phenyl-1-methyl-3:4-dihydroquinoxaline)][2-(1:3:3-trimethylindoline)]trimethincyanine** chloride, 397.

**4-Keto-1-phenyl-1:2:3:4-tetrahydro-2-naphthoic acid,** 3-bromo-, 13.
**4-Keto-1:2:3:4-tetrahydro-2-naphthoic acid,** 3-bromo-, 7-chloro-, and 7-chloro-3-bromo-, 12.

L.

**Lauric aldehyde,** preparation of, 86.
**Lead,** bivalent, co-ordination number of, 661.
**Lead nitrate,** compound of, with thiourea, 661.
**Lead determination :—**
determination of, in brass, volumetrically, 41.
**Lectures,** delivered before the Chemical Society, 328, 629.
**Linolenic acid,** ethyl ester, 546.
**Lithium** halides, ammines and deuterammines of, 118.
**Liversidge Lecture,** 328.
**Lutidylquinolines,** and their picrates, 415.
**Lycoctonine,** 141.

M.

**Magnetochemistry,** 328.
**Maleic anhydride,** reaction of, with anthranil, 654.
**Malondiamidine** *di*hydrochloride, 575.
**Malondi-iminoether** *di*hydrochloride, 575.
**Malonic acid,** derivatives of, reactions of, with amidines, 388.
**Mandelic acid,** and its derivatives, physical constants of active and racemic forms of, 227.
effect of heat on, 249.
*r* and *l*-**Mandelic acids,** solubilities of, in water, 231.
**Manganous** chloride, ammines and deuterammines of, 118.
**4-*d*-Mannosidamino-2-methylthiopyrimidine,** 6-amino-, and its acetyl derivatives, 573.
**Melanthigenin,** constitution of, 70.
**Mercury alloys** with rare-earth metals, 8, 531.
**Mesitylenesulphonamidoacetic acid,** ethyl ester, 377.
***N*-Mesitylenesulphonyl-*N*-β-methylallylglycine,** 377.
**Mesitylsulphonylalanine,** and its ethyl ester, 378.
**Metals** of the aluminium group, analysis of, 72.
**Metal ammines,** dissociation pressures of, 104.
**Metallic salts,** compounds of, with ammonia and trideuterammonia, dissociation pressures of, 104.
**Methacrylic acid,** synthesis of, and its ethylene and *n*-hexyl esters, 238.
**Methenylbiscyanoacetic acid,** ethyl ester, 390.
**5-Methoxy-4-acetamidobenzeneazo-β-naphthol,** 2:3:6-*tri*chloro-, 237.
**4-Methoxyacetophenone,** 2-bromo-, semicarbazone, 526.
**7-Methoxyacridine,** 2-chloro-5-amino-, 654.
**6-Methoxybenzeneazo-2′-hydroxy-3′-naphthanilide,** 2:3:5-*tri*chloro-4-nitro-, 237.
**4-Methoxybenzeneazo-β-naphthol,** 2:3:5:6-*tetra*chloro-, 234.
**6-Methoxybenzeneazo-β-naphthol,** 2:3:5-*tri*chloro-, 2:3:4:5-*tetra*chloro-, 2:3:5-*tri*chloro-4-bromo- and -6-hydroxy-, 236.
**6-Methoxy-*p*-benzoquinone,** 2:3:5-*tri*chloro-, 236.
**4-Methoxybenzylsuccinic acid,** and its anhydride, 12.
**6-Methoxy-2:4-bis*tri*chloromethyl-1:3-benzdioxin,** 5:7-*di*chloro-, 320.
**6-Methoxy-2:4-bis*di*chloromethylene-1:3-benzdioxin,** 5:7-*di*chloro-, 320.
**6-Methoxy-2-carbomethoxy-2:5-dimethyltetralin-1-acetic acid,** 1-hydroxy-, methyl ester, 494.
**4-Methoxy-7:8-dihydro-1:2-*cyclo*pentenonaphthalene-3′-acetic acid,** 500.
**6-Methoxy-3:5-dimethyl-3:4-dihydronaphthalene-1-acetic acid,** 495.
**2-Methoxy-1:5-dimethylnaphthalene,** 493.
**6-Methoxy-2:5-dimethyltetralin-1-acetic acid,** 496.
**6-Methoxy-2:5-dimethyl-1-tetralone,** and its 2:4-dinitrophenylhydrazone, 494.
**6-Methoxy-2:5-dimethyl-1-tetralone-2-carboxylic acid,** methyl ester, 494.
**4-Methoxy-2′-hydroxy-3′-naphthanilide,** 2:3:5:6-*tetra*chloro-, 235.
**4-Methoxy-3-methylacetophenone,** 6-chloro-, 500.
**4-Methoxy-2-methylbenzeneazo-β-naphthol,** 223.
**4-Methoxy-2-methylbenzenediazoaminocarbonamide,** 223.
**2-Methoxy-4-methylbenzoylacetone,** 434.
**α-2-Methoxy-4-methylbenzoyl-α-*n*-amylacetone,** 435.
**α-2-Methoxy-4-methylbenzoyl-α-benzylacetone,** 435.
**α-2-Methoxy-4-methylbenzoyl-α-*n*-butylacetone,** 435.
**α-2-Methoxy-4-methylbenzoyl-α-ethylacetone,** 434.
**α-2-Methoxy-4-methylbenzoyl-α-methylacetone,** 434.
**α-2-Methoxy-4-methylbenzoyl-α-*n*-propylacetone,** 434.
**4-Methoxy-3-methyldiazoaminobenzene,** 4′-nitro-, 223.
**4-Methoxy-3-methylhydrazobenzene-*N*-diazocarbonamide,** 223.
**4-Methoxy-1-methyl-2-naphthoic acid,** methyl ester, 13.
**6-Methoxy-5-methyltetralin,** 493.
**6-Methoxy-5-methyl-1-tetralone,** and its 2:4-dinitrophenylhydrazone, 493.
**6-Methoxy-5-methyl-1-tetralone-2-carboxylic acid,** methyl ester, and its 2:4-dinitrophenylhydrazone, 494.
**6-Methoxy-5-methyl-1-tetralone-2-glyoxylic acid,** methyl ester, 493.
**6-Methoxy-2-naphthoic acid,** 4-hydroxy-, 12.
**6-Methoxy-*N*-nitroaniline,** 2:3:5-*tri*chloro-4-nitro-, 236.
**4-Methoxy-1:2-*cyclo*pentadienonaphthalene-3′-acetic acid,** 499.
**4-Methoxy-1:2-*cyclo*pentenonaphthalene-3′-acetic acid,** 499.
**α-(β-*p*-Methoxyphenylacrylyl)tetronic acid,** 242.
**3-*m*-Methoxyphenyl-$\Delta^2$-*cyclo*penten-1-one-2-acetic acid,** 499.
**Methoxyphenylpyridines,** and amino-, and nitro-, and their derivatives, 410.
**5-Methoxypyridine,** β-2-nitro-, 411.
**Methoxypyridylquinolines,** and their picrates, 410.
**6-Methoxy-8-α-pyridylquinoline,** 5-amino-, and 5-nitro-, 411.
**6-Methoxyquinoline,** 5-amino-, 410.
**5-(6′-Methoxyquinolyl-8′-γ-aminopropylamino)-7-methoxyacridine,** and its dihydrochloride, 556.
**Methoxyquinolyl-2:5-dimethylpyrrole-3:4-dicarboxylic acids,** ethyl esters, 420.
**1-6′-Methoxy-8′-quinolyl-2:5-pyrrole,** 420.
**4′-Methoxy-2-styryl-3-benzyl-7-methylchromone,** 435.
**4′-Methoxy-2-styryl-3:7-dimethylchromone,** 434.
**4′-Methoxy-2-styryl-7-methylchromone,** 434.
**4′-Methoxy-2-styryl-7-methyl-3-ethylchromone,** 434.
**2-(6′-Methoxy-*m*-tolyl)furan-5-β-propionic acid,** 2-4′-chloro-, 500.
**Methyl alcohol,** action of, on *m*-toluidine hydrochloride, 14.
**Methyl** ether, free energy of, from equilibrium with methyl alcohol, 589.
**10-Methylacridane,** 5-amino-5-hydroxy-, and 5-imino-, 460.
**5-Methylacridine** metho-*p*-toluenesulphonate, 6.
**5-Methylacridine,** 3-*mono*- and 3:7-*di*-amino-, and 3-nitro-7-amino-, and their derivatives, 346.
**5-Methylacridines,** 344.
**10-Methylacridinium** bromides, amino-, 460.
**2-Methyladenine,** and its picrate, 385.
***N*-β-Methylallylglycine,** *N*-benzene- and -toluene-sulphonyl derivatives, 377.
**5-Methylaminoacridine,** 461.
**4-Methylaminoanthraquinone-2-sulphonic acid,** 1-amino-, sodium salt, 47.
**4-Methylamino-2-methylthiopyrimidine,** 6-amino-, 385.
**8-γ-Methylaminopropylamino-6-methoxyquinoline,** and its salts, 562.
**4-Methylamino-5-thioformamido-2-hydroxy-6-methylpyrimidine,** 385.
**4-Methylamino-5-thioformamido-2-methylthiopyrimidine,** 6-amino-, 385.
**2-Methyl-3-*n*-amylquinoxaline,** and its *di*-*N*-oxide, 325.
**Methylaniline,** 2:3:5:6-*tetra*chloro-*N*-*mono*- and -*N*:4-*di*-nitro-, 373.
**β-(*N*-Methylanilino)anethole,** 611.
**[2-(1-Methylbenzthiazole)][2-(3-keto-1:4-dimethyl-3:4-dihydroquinoxaline)]methincyanine** iodide, 399.
**[2-(1-Methylbenzthiazole)][2-(1-phenyl-3-methylquinoxaline)]-methincyanine** iodide, 399.
**6-Methyl-2:4-bis*tri*chloromethyl-1:3-benzdioxin,** 8-amino- and 7- and 8-nitro-, 320.
**6-Methyl-2:4-bis*di*chloromethylene-1:3-benzdioxin,** 8-amino-, and 7-nitro-, 320.
**4-Methylbenzylsuccinic acid,** and its anhydride, 12.
**6-Methylcarvomenthone,** 502.
**Methyl*di*chloroarsine,** preparation of, 549.
**2-Methyl-5-*n*-decylpentadecoic acid,** 618.
**Methyl-*n*-decyl-*n*-dodecylacetic acid,** and its amide, 617.
**β-Methyl-β-*n*-decyl-β-*n*-dodecylpropionic acid,** and its amide and methyl ester, 618.
**2-Methyldiazoaminobenzene,** 4′-nitro-4-hydroxy-, 223.

**Methyldi-*n*-heptylacetic acid**, and its amide, 618.
**2-Methyldihydro-1:3-thiazine**, and its derivatives, 247.
**[2-(3-Methyldihydro-1:3-thiazine)][2-(6-acetamido-3-ethylbenzthiazole)]methincyanine** iodide, 248.
**[2-(3-Methyldihydro-1:3-thiazine)][2-(6-chloro-3-ethylbenzthiazole)]methincyanine** iodide, 248.
**[2-(3-Methyldihydro-1:3-thiazine)][2-(3-ethyl-6:7-benzbenzoxazole)]methincyanine** iodide, 247.
**[2-(3-Methyldihydro-1:3-thiazine)][2-(3-ethylbenzoxazole)]trimethincyanine** iodide, 249.
**[2-(3-Methyldihydro-1:3-thiazine)][2-(3-ethylbenzselenazole)]methincyanine** iodide, 248.
**[2-(3-Methyldihydro-1:3-thiazine)][2-(3-ethylbenzthiazole)]methincyanine** iodide, 248.
**[2-(3-Methyldihydro-1:3-thiazine)][2-(3-ethylbenzthiazole)]trimethincyanine** iodide, 249.
**[2-(3-Methyldihydro-1:3-thiazine)][2-(1-ethylquinoline)]methincyanine** iodide, 248.
**[2-(3-Methyldihydro-1:3-thiazine)][4-(1-ethylquinoline)]methincyanine** iodide, 248.
**[2-(3-Methyldihydro-1:3-thiazine)][2-(3-methyl-4:5-benzbenzthiazole)]methincyanine** iodide, 247.
**[2-(3-Methyldihydro-1:3-thiazine)][2-(3-methyl-6:7-benzbenzthiazole)]methincyanine** iodide, 247.
**[2-(3-Methyldihydro-1:3-thiazine)][2-(3-methylbenzthiazole)]methincyanine** iodide, 247.
**[2-(3-Methyldihydro-1:3-thiazine)][2-(1-methylquinoline)]methincyanine** iodide, 248.
**[2-(3-Methyldihydro-1:3-thiazine)][4-(1-methylquinoline)]methincyanine** iodide, 248.
**3-Methyl-2-*n*-dodecyl-lauric acid**, 618.
**4-Methyl-3-*n*-dodecyltridecoic acid**, 618.
**Methylenecyanoacetic acid**, amino-, ethyl ester, 390.
**β-3:4-Methylenedioxyphenyl*iso*propylamine**, preparation of, 15.
**Methyl-*n*-heptyl-*n*-tetradecylacetic acid**, 618.
**12-Methyl-1:2:3:4:12:13-hexahydroxanthen**, 475.
**1-Methyl*cyclo*hexane-1-acetamide**, 502.
**1-Methyl*cyclo*hexane-1-cyanoacetic acid**, ethyl ester, 502.
**1-Methyl*cyclo*hexene**, 475.
chlorination of, 296.
**2-Methylhex-3-en-5-yn-2-ol**, and its phenylurethane, 263.
**3-Methylhex-3-en-5-yn-2-ol**, and its α-naphthylurethane, 263.
**1-Methylindole**, 5:6-*di*hydroxy-, and 2-iodo-5:6-*di*hydroxy-, diacetyl derivatives, 48.
**Methyl-lycaconitine**, and its hydriodide, 140.
**Methyl β-methylgalactosides**, 53.
**6-Methyl-2-morpholone**, *N*-benzene- and -toluene-sulphonyl derivatives, 376.
**2-Methyl*peri*naphtha-1:3-thiazine**, and its derivatives, 489.
**1-Methyl-2-naphthoic acid**, 4-hydroxy-, and its derivatives, 13.
**6-Methyl-2-naphthoic acid**, 4-hydroxy-, 12.
**7-Methylnona-2:7-dien-5-yn-4-ol**, and its α-naphthylurethane, 267.
**7-Methylnona-3:7-dien-5-yn-2-ol**, and its α-naphthylurethane, 267.
**7-Methylnonan-2-ol**, and its 3:5-dinitrobenzoate, 267.
**7-Methylnonan-4-ol**, and its 3:5-dinitrobenzoate, 267.
**7-Methylnonan-2-one**, and its derivatives, 267.
**7-Methylnonan-4-one**, and its phenylsemicarbazone, 267.
**7-Methylnon-7-en-5-yn-4-ol**, and its derivatives, 267.
**Methyl-*n*-nonyl-*n*-dodecylcarbinol**, 618.
**3-Methylpent-2-en-4-yne**, condensation of, with butaldehyde, citral, and crotonaldehyde, 265.
**ψ-2-Methyl-1-γ-phthalimidopropylquinolinium** bromide, 6-amino-, acetyl derivative, 560.
**8-γ-Methylpropylaminopropylamino-6-methoxyquinoline**, and its salts, 564.
**2-Methylpyrimidine**, 4:6-*di*amino-, 4:5:6-*tri*amino-, 5-thioformyl derivative, 4:6-*di*chloro-, and 4-chloro-6-amino-, 385.
4:5-*di*amino-6-hydroxy-, 5-thioformyl derivative, 384.
**2-(3-Methyl-4-quinazolonyl)-3-(2-ketodihydroquinoxalyl)methane**, 400.
**2-(3-Methyl-4-quinazolonyl)-3-(2-keto-1-methyldihydroquinoxalyl)methane**, 400.
**2-(3-Methyl-4-quinazolonyl)-3-(2-keto-1-phenyldihydroquinoxalyl)methane**, 400.
**3-Methyl-4-quinazolonyl-2-pyruvic acid**, ethyl ester, and its phenylhydrazone, 400.
**2-Methylquinoxaline *di*-*N*-oxide**, 324.
**[2-(1-Methylquinoxaline)][(4-dimethylaminophenyl)]dimethincyanine** iodide, 2-3-hydroxy-, 396.
**[2-(1-Methylquinoxaline)][2-(1-methylbenzoxazole)]trimethincyanine** iodide, 2-3-hydroxy-, 396.
***l*-Methylsuccinylanthranilic acid**, 141.
**2-Methyl-1:2:3:4-tetrahydro*iso*arsinoline**, and its derivatives, 549.
**5:2′-(3′-Methyltetrahydrothiazolyl)ethylidene-3-ethylrhodanine**, 249.
**5:2′-(3′-Methyltetrahydro-1′:3′-thiazyl)ethylidene-3-ethylrhodanine**, 249.
**5-Methyltetralin**, 6-hydroxy-, 493.
**Methylthiazylquinolines**, 419.
**2-Methylthioadenine**, 385.
**2-Methylthiodihydro-1:3-thiazine**, and its methiodide, 246.
**2-Methylthio-9-methyladenine**, 385.
**2-Methylthio-9-methylpurine**, 6-hydroxy-, 386.
**2-Methylthiopyrimidine**, 4:6-*di*amino-, acetyl derivative and picrate, 573.
4:5:6-*tri*amino-, and its 5-thioformyl derivatives, 385.
**Methyl vinyl ketone**, polymerisation and preparation of, 25.
**Moss**, carragheen. See Carragheen moss.
Iceland. See Iceland moss.
**Moulds**, metabolites from, behaviour of, at dropping mercury cathodes, 133.

## N.

**Naphthalene**, 1:3:5:7-*tetra*amino-, and *tetra*nitro-derivatives, 33.
1-bromo-2- and -4-iodo-6-nitro-, 1-bromo-6- and -7-nitro-, 1:2- and 1:4-*di*bromo-6-nitro-, 1-chloro-6-nitro-, and 1-iodo-6-nitro-, 392.
*di*nitro-derivatives, monoreduction of, 318.
1:3-*di*nitro-, preparation of, 433.
1:6-*di*nitro-, preparation of, 86.
2:3-*di*nitro-, preparation of, 635.
**Naphthalene-1-azo-β-naphthol**, 6-nitro-, 392.
**Naphthalene-1:2-diazo-oxide**, 4-chloro-, 4-iodo-, and 4-nitro-, 322.
**3′-Naphthanilide**, 2:3:5:6-*tetra*chloro-2′-hydroxy-, and 2:3:5:6-*tetra*chloro-4-nitro-2′-hydroxy-, 234.
**2-Naphthoic acid**, 7-chloro-4-hydroxy-, 12.
4-halogeno-derivatives, and 4-nitro-, 468.
**α-Naphthol**, methylation of, nuclear, 168.
**2-Naphthyl** methyl ethers, 4-bromo-, 4-chloro-, and 4-iodo-, 469.
**1-Naphthylamine**, 2:4-*di*bromo-6-nitro-, 2:4-*di*chloro-6-nitro-, 4-iodo-6-nitro-, 2:6- and 4:6-*di*nitro-, and 2:4:6-*tri*nitro-, 393.
6-nitro-, diazo-coupling, halogenation, mercuration, and nitration of, 391.
4-mercuriacetate, 393.
picrate, 391.
2:3-*di*nitro-, 635.
2:4-*di*nitro-, preparation of, 433.
**2-Naphthylamine**, 3-nitro-, and its picrate, 636.
**1-β-Naphthyl-3:3-dimethyltriazen**, 444.
**1:4-Naphthylenediamine**, 2:3-*di*nitro-, preparation of, 636.
**6-Naphthyl-1-maleamic acid**, 6-nitro-, 391.
**Nickel**, catalytic reduction by formic acid with, 281.
**Nickel** chloride, ammines and deuterammines of, 118.
*Nigella sativa*, melanthigenin from, 70.
**Ninhydrin**, properties of, 72.
**Nitric acid**. See under Nitrogen.
**Nitrogen compounds**, optically-active, tervalent, preparation of, 659.
**Nitric acid**, transport numbers of, in water, 647.
**Nitrogen organic compounds**, heterocyclic, 658.
***n*-Nonyloxybenzoic acid**, 432.
**Nor-α-amyradienonyl** acetate, 524.

## O.

**Obituary Notices :—**
Randal Thomas Mowbray Rawdon Berkeley, Earl of Berkeley, 503.
John William Blagden, 334.
Alfred Archibald Boon, 507.

Sir Bryce Chudleigh Burt, Kt., 200.
Francis William Clifford, 201.
Samuel Felix Dufton, 508.
Frank William Harbord, 202.
Arthur Harden, 334.
Matthew Hunter, 43.
Alfred Hutchinson, 340.
Ivan Douglas Lamb, 202.
Grace Cumming Leitch, 341.
Herbert Marsden, 341.
Joseph William Mellor, 341.
Colin Richard Morrison-Jones, 343.
Walter Odling, 43.
Harold Gordon Rule, 509.
Frank Sturdy Sinnatt, 203.
Raymond Taylor, 510.
Reece Henry Vallance, 44.
William John Young, 44.
**n-Octyloxybenzoic acid**, 432.
**Oleic acid**, methyl ester, hydro*per*oxide and *per*oxide, 119.
oxidation of, and of its methyl ester by hydrogen peroxide in acetic acid, 37.
**Organic compounds**, analysis of, micro-, 313.
molecular, formation and structure of, 462.
spectra of, absorption, in solution, effect of molecular environment on, 565.
**Oxalic acid**, dysprosium, erbium, ytterbium, and yttrium salts, 40.
**Oxaloacetic acid**, ethyl ester, diphenylenehydrazone, 660.
**9:10-Oxidostearic acids**, stereochemistry of, 204.

P.

**Palladium bases**, interchange of hydrogen in, with deuterium oxide, 367.
**Parachors** of organic compounds, 146.
**Phenacylaniline**, and *p*-chloro-, and their derivatives, 63.
**Phenacylarylamines**, indole formation from, 58.
**Phenacyl-*N*-*iso*butylaniline**, *p*-chloro-, 65.
**Phenacyl-2:4-dimethylaniline**, *p*-chloro-, 63.
**Phenacyl-*N*-ethylaniline**, and its salts, 65.
**Phenacyl-*N*-ethylaniline**, *p*-chloro-, and its salts, and *p*:*p*′-*di*chloro-, 65.
**Phenacyl-*N*-ethyl-*p*-toluidine**, 65.
**Phenacyl-*N*-ethyl-*p*-toluidine**, *p*-chloro-, and its salts, 65.
**Phenacyl-*N*-methylaniline**, *p*-chloro-, 65.
**Phenacyl-*p*-toluidine**, *p*-chloro-, 63.
**5:6:9′:10′-Phenanthraphenazine**, 1:2:4-*tri*chloro-, *di*chloro-amino-derivatives, and 1:2:4-*tri*chloro-3-amino-, 576.
**Phenol**, reaction of, with aluminium chloride, 527.
spectrum of, absorption, ultra-violet, 380.
**Phenol**, 2:3:5:6-*tetra*chloro-4-nitro-, and its acetate, 235.
3-fluoro-4-nitroso-, spectrum of, absorption, 89.
*p*-nitroso-, tautomerism of, in systems with benzoquinone, 89.
**Phenols**, condensation of, with ketones, 486.
nitrosation of, 221.
reaction of, with aluminium chloride, 527.
*m*-substituted, spectra of, absorption, ultra-violet, 380.
**Phenyl benzyl ethers**, *m*-chloro-, *di*chloro-, and *m*-fluoro-, 432.
esters, reaction of, with phosphorus pentoxide, 79.
ethers, halogenation of, 430.
selenide, physical constants of, 22.
sulphide, physical constants of, 22.
***N*-γ-Phenoxypropyl-β-aminoethylaniline**, 2:4-*di*nitro-, and its hydrochloride, 556.
**Phenylacetamidoethanesulphonic acid**, sodium salt, 5.
**Phenylacetic acid**, *p*-nitro-, anhydride, 69.
**Phenylacetylmalonic acid**, *p*-nitro-, ethyl ester, and its sodium derivative, 69.
**α-Phenyl-β-5-acridylethanol**, α-nitro-derivatives, 6.
**α-(β-Phenylacrylyl)tetronic acid**, 242.
**α-Phenylallylene**, α-*p*-nitro-, 70.
α-2:4-*di*nitro-, 70.
**Phenyl-2-aminophenylallylcarbinol**, and its derivatives, 451.
**α-Phenyl-α-(2-aminophenyl)-β-benzylethylene**, 451.
**α-Phenyl-α-(2-aminophenyl)-β-(1′-naphthyl)ethylenes**, 449.
**Phenyl-2-aminophenyl-β-phenylethylcarbinol**, and its *N*-acetyl derivative, 450.
**α-Phenyl-$\Delta^{\alpha}$-amylene**, β-chloro-, 69.
**Phenylanisylpyrroles**, 594.
**2-Phenyl-4-*p*-anisylpyrrole-5-aldehyde**, and its oxime, 597.
**Phenylanisylpyrrolines**, and their picrates, and 5-nitroso-, 594.
**Phenylbenzyl-2-aminophenylcarbinol**, 450.
**2-Phenyl-3-benzylcinnoline**, 451.
**Phenylbromoacetic acid**, sodium salt, hydrolysis of, 80.
**α-Phenyl-$\Delta^{\alpha}$-butylene**, β-chloro-, 69.
**2-Phenyl-1-*iso*butylindole**, 2-*p*-chloro-, and 2-*p*-chloro-3-nitroso-, 68.
3-*p*-chloro-, 66.
**β-Phenylbutyrophenone**, γ-nitro-, oxime, 595.
γ-nitro-β-*m*-hydroxy-, 593.
γ-nitro-β-*m*-nitro-, 592.
**9-Phenylcarbazole**, 1- and 9-2′-amino-, and 1- and 3-nitro-, 661.
**Phenylchloroacetic acid**, sodium salt, hydrolysis of, 80.
**2-Phenyl-2-*p*-chlorophenacyl-1:2:3:4-tetrahydro*iso*arsinolinium** salts, optically active, 554.
***dl*-2-Phenyl-2-*p*-chloro-1:2:3:4-tetrahydro*iso*arsinolinium** bromide and iodide, preparation and resolution of, 550.
**2-Phenylchrysene**, 450.
**2-Phenyl-3:4:6:7-dibenzo-1:5-naphthyridine**, and its picrate, 318.
**β-Phenyl-αα-di-(*p*-ethoxyphenyl)ethylene**, and β-bromo-, 394.
**β-Phenyl-αα-dimethyl-*n*-butyric acid**, and its methyl ester, 429.
**γ-Phenyl-αα-dimethyl-$\Delta^{\beta}$-butyrolactone**, 428.
**2-Phenyl-5:7-dimethylindole** picrate, 64.
**4-Phenyl-2:6-dimethylpyridine**, 4-*p*-amino-, 416.
**4-Phenyl-2:6-dimethylpyridine-3:5-dicarboxylic acid**, 4-*p*-amino-, and 4-*p*-nitro-, ethyl esters, 416.
**1-Phenyl-3:3-dimethyltriazen**, and 1-*m*- and -*p*-nitro-, 443.
**1-Phenyl-3:3-dimethyltriazen-3′:4′-dicarboxyimide**, 444.
**1-Phenyl-3:3-dimethyltriazen-3′:4′-dicarboxylic acid**, methyl ester, 444.
**α-Phenyl-αβ-diphenylethylenes**, α-2-amino-, 450.
**α-Phenyl-β-(2:4-diphenyl-5-pyrrolyl)ethylene**, α-2:4-*di*nitro-, 597.
**1:9-Phenylenecarbazole**, 660.
***m*-β-Phenylethoxybenzoic acid**, 432.
**2-Phenyl-1-ethylindole**, 2-*p*-chloro-, 2-*p*-chloro-3-nitroso-, and 3-nitroso-, 67.
**3-Phenyl-1-ethylindole**, and 3-*p*-chloro-, 66.
**Phenyl-*N*-ethylnitrosoamine**, *p*-chloro-, 67.
**α-Phenyl-β-(2-furyl)ethylenes**, α-nitroamino-, and their *N*-acetyl derivatives, 451.
**β-Phenylhexophenone**, γ-nitro-, 595.
**β-Phenyl-*p*-methoxybutyrophenone**, γ-nitro-, 593.
**2-Phenyl-5-methyl-1-ethylindole**, and 2-*p*-chloro-, 67.
**3-Phenyl-5-methyl-1-ethylindole**, and 3-*p*-chloro-, and their picrates, 66.
**2-Phenyl-5-methylindole**, 2-*p*-chloro-, and chloronitroso-, 64.
**3-Phenyl-1-methylindole**, 3-*p*-chloro-, and its picrate, 66.
**1-Phenyl-3-methylquinoxaline-2-aldoxime** chloride, 400.
**2-Phenylnaphthalene**, 1:3-*di*hydroxy-2-2′:4′-*di*nitro-, 69.
**4-Phenyl-3-(1′-naphthyl)cinnoline**, 450.
**α-Phenyl-β-5-(3-nitroacridyl)ethanol**, α-*o*- and -*m*-nitro-, 347.
**β-Phenylpropionamidoethanesulphonic acid**, sodium salt, 5.
**α-(β-Phenylpropionyl)tetronic acid**, 242.
***m*-γ-Phenyl-*n*-propoxybenzoic acid**, 432.
**8-β′-Phenyl*iso*propyl-γ-aminopropylamino-6-methoxyquinoline**, and its salts, 563.
**α-Phenyl-$\Delta^{\alpha}$-propylene**, β-chloro-α-*p*-nitro-, and -α-2:4-*di*nitro-, 70.
**2-Phenyl-1-*n*-propylindole**, 2-*p*-chloro-, and 2-*p*-chloro-3-nitroso-, 68.
**Phenylpyridines**, *o*-amino-, and their benzoyl derivatives, and their picrates, 317.
**α-Phenylpyridine**, α-3-amino- and α-3-nitro-4-hydroxy-, 412.
3:4-*di*amino-, and 3-nitro-4-amino-, and its acetyl derivative, 405.
**β-Phenylpyridine**, 3:4-*di*amino-, and 3-nitro-4-amino-, and its acetyl derivative, 413.
**γ-Phenylpyridine**, 3-hydroxy-, 411.
**2-Phenyl-6-pyridylquinoline-4-carboxylic acids**, 412.
**Phenylpyruvic acid**, 2-nitro-5-hydroxy-, benzyl derivative, and its phenylhydrazone, 49.
**5-Phenylquinoline**, and its picrate, 444.
**Phenylquinolines**, amino-, and their derivatives, 317.
**2-Phenylquinoline-4-carboxylic acid**, 3-amino-, benzoyl derivative, 318.

**2-Phenyl-1:2:3:4-tetrahydro*iso*arsinoline**, and its derivatives, 549.
**2-Phenyl-1:2:3:4-tetrahydro*iso*phosphinoline**, and its methiodide, 550.
**β-Phenyl-αaββ-tetramethylpropionic acid.** See β-Phenyl-αaβ-trimethyl-*n*-butyric acid.
**β-Phenyl-αaβ-trimethyl-*n*-butyric acid**, and its derivatives, 428, 429.
**γ-Phenyl-αaβ-trimethylbutyrolactone**, 428.
**γ-Phenyl-αaβ-trimethyl-Δ^β^-butyrolactone**, 428.
**β-Phenyl-αaβ-trimethylpropionic acid.** See β-Phenyl-αa-dimethyl-*n*-butyric acid.
**α-(δ-Phenylvaleryl)tetronic acid**, 242.
**Phosphorus *penta*chloride**, action of, on *as*-substituted acetones, 68.
*penta*xide, reaction of, with phenyl esters, 79.
**Photochemical** reactions, 275, 276.
**Phthalaz-1:4-dione**, 6-chloro-, 659.
**8-ω-Phthalimidodecylamino-6-methoxyquinoline**, and its hydrochloride, 558.
**8-β-Phthalimidoethyl-6-methoxyquinoline**, 555.
**8-γ-Phthalimidopropylamino-6-methoxyquinoline**, preparation of, 557.
**5-γ-Phthalimidopropylamino-(*N*-6′-methoxy-8′-quinolyl)-7-methoxyacridine**, 2-chloro-, 556.
**8-γ-Phthalimidopropyl-γ-aminopropylamino-6-methoxyquinoline *di*hydrobromide**, 556.
**4-Phthalo-3-amino-*p*-anisidide**, 411.
**Phthalo-ω-bromodecylimide**, 558.
**Phthalo-γ-(γ-bromopropylamino)propylimide** hydrobromide, 556.
**4-Phthalo-3-nitro-*p*-anisidide**, 411.
**Phthalo-γ-(γ-phenoxypropylamino)propylimide** hydrobromide, 555.
**Phthioic acid**, constitution and synthesis of, 615.
**Physical** properties, constitution and, 16, 636.
**Picryl** halides, molecular compounds of, with hexamethylbenzene, 435.
**6-Piperonylidene-2:2-dimethyl*cyclo*hexanone**, 662.
**6-Piperonylidene-2-methyl-2-ethyl*cyclo*hexanone**, 662.
**6-Piperonylidene-2-methyl*cyclo*hexanone**, 662.
**Platinum bases**, interchange of hydrogen in, with deuterium oxide, 367.
**Polarography**, 133.
**Polyene series**, 261, 264, 265, 268.
**Polyisoprenes**, 289, 472.
autoxidation in, 119, 122, 125, 356, 541.
**Polymethylbenzoylnaphthoic acids**, 239.
**Polysulphanilamides**, 606.
**Potassium organic compounds**:—
**Potassium** ferrocyanide, commercial, colour variation in, 223.
**Propane**, α-amino-γ-hydroxy-, and its α-acetyl derivative, 247.
**Propenylethynylcarbinol**, isomerisation of, 261.
**Propionic acid**, α-amino-, ethyl ester, *p*-toluenesulphonyl derivative, 378.
β-cyano-, preparation of, and its dissociation constant, 516.
**Propionyl-*r*-mandelic acid**, solubility of, in water, 231.
***O*-Propionyl-*r*- and -*l*-mandelic acids**, 228.
**Propiophenone**, *p*-hydroxy-, benzoyl derivative, 612.
***iso*Propoxybenzoic acid**, 432.
**Propylalanine**, β-hydroxy-, 378.
**Propylamine**, β-hydroxy-, derivatives of, 377.
**8-Propylamino-6-methoxyquinoline**, 8-γ-amino-, meconate, 557.
8-γ-chloro- and 8-γ-hydroxy-, 561, 562.
**8-γ-Propylaminopropylamino-6-methoxyquinolines**, and their salts, 562.
**8-Propyl-γ-aminopropylamino-6-methoxyquinoline**, 8-γ-amino-, *tri*hydrochloride, 556.
8-γ′-amino-, and its salts, 564.
**8-Propylaminoquinoline**, 8-γ-cyano-, 560.
***N*-Propylglycine**, *N*-βγ-*di*bromo-, derivatives of, 378.
***dl*-*N*-Propylglycine**, *N*-β-hydroxy-, and its *N*-*p*-toluenesulphonyl derivative, 376.
**Pschorr reaction**, effect of substitution on, 447.
**Purine nucleosides**, synthesis of, 383, 571, 574.
**4-Pyridylacetoacetanilides**, 413.
**Pyridylacridines**, 417.
**Pyridylacridones**, 418.
**8-Pyridyl-5-*tert.*-butylquinoline**, 412.
**4-Pyridyldiphenylamine**, and its picrate, 418.
**Pyridyldiphenylamine-2′-carboxylic acids**, 418.
**6-β-Pyridyl-2:3-diphenylquinoxaline**, 413.
**2-Pyridylnaphthalenes**, and their picrates, 444.
**4-Pyridylphthalimides**, 444.
**6-α-Pyridyl-8-α(β and γ)-pyridylquinoline**, 405.
**6-Pyridylquinaldines**, 412.
**Pyridylquinolines**, and their derivatives, 401.
**5-α-Pyridylquinoline**, 8-hydroxy-, 412.
**6-α-Pyridylquinoline**, 8-amino-, and 8-nitro-, 405.
**6-β-Pyridylquinoxaline**, 413.
**Pyrimidine**, 4:6-*di*amino-, preparation of, and 4:6-*di*chloro-, 574.
4:5:6-*tri*amino-, and its 5-thioformyl derivative, 387.
4-amino-5-cyano-, and its picrate, 387.
4:6-*di*hydroxy-, 389.
***l*-Pyrrolidone**, 3-amino-, and its derivatives, 40.
**Pyruvic acid**, and its methyl ester, diphenylenehydrazones of, 660.

## Q.

**Quinoline**, 5-chloro-, picrate, 444.
**Quinoline series**, therapeutic agents of, 401, 404, 406, 413, 417, 419.
**Quinolinealdehydes**, 415.
**Quinolineamidines**, and their salts, 420.
**Quinolinecarboxyhydrazides**, and their *p*-toluenesulphonyl derivatives, 415.
**Quinolinecarboxylic acids**, ethyl esters, and their toluenesulphonyl derivatives, 415.
**Quinolinethioamides**, 419.
**4-Quinolyl-2:6-dimethyldihydropyridine-3:5-dicarboxylic acids**, ethyl esters, 414.
**4-Quinolyl-2:6-dimethylpyridine-3:5-dicarboxylic acids**, ethyl esters, 415.
**1-3′-Quinolyl-2:5-dimethylpyrrole**, 420.
**1-Quinolyl-2:5-dimethylpyrrole-3:4-dicarboxylic acids**, ethyl esters, 420.
**1-(5′-Quinolyl)-3:3-dimethyltriazen**, 444.
**Quinones**, polarography of, 133.
**Quinoxaline *di*-*N*-oxide**, 324.
**Quinoxaline cyanines**, 394, 397.

## R.

**R. 63**, constitution of, 555.
preparation of, and its salts, 557.
**Racemates**, stability of, 227.
**Reactions**, kinetic theory of, in solution, 629.
**Report of the Council**, 171.
**Resins, synthetic**, formaldehyde–phenol, combination of, with olefines and with rubber, 472.
**Resinols**, triterpene, 523.
**Resorcinol**, spectrum of, absorption, ultra-violet, 381.
***d*-Ribobenziminazole**, 628.
**Rosmarinecine**, and its methiodide, 453.
**Rosmarinine**, 452.
**Rubber**, 289, 472.
autoxidation of, 546.
oxidation of, in presence of acetic acid or its anhydride, 356.
peroxidation of, 125.

## S.

**Saccharin**, 5-amino-, acetyl derivative, 78.
**2-Salicylideneaminoacridine**, 460.
**Saligeninodihydromyrcene**, 476.
**Saligenino-rubber**, 476.
**Salts**, complex, interchange of hydrogen isotopes with, 361, 367.
**Scheelite**, rare earths in, 577.
**Senecic acid**, 454.
*Senecio*, alkaloids from, 452.
**Sitosterol**, oxidation of, 599.
**Sodium** iodide, ammine and deuterammine of, 118.
**Sodium organic compounds**:—
**Sodium** ferrocyanide, commercial, colour variation in, 223.

**Solvents**, hydroxylic, reaction of, with alkyl halides, 255.
**Spasmolytics**, 401.
**Spectra**, absorption, of organic compounds in solution, effect of molecular environment on, 565.
**Squalene**, autoxidation of, 546.
**Starch**, amylolysis of, 619.
**Stearic acid**, 9:10-*di*hydroxy-derivatives, configuration of, 37, 204.
**Stereochemistry** of labile compounds, 194.
**Steroids**, acyl migration in, 135.
**Sterols**, synthesis of substances related to, 491, 497.
**Sterol group**, 599, 602.
acyl migrations in, 437.
**Stilbene**, derivatives, preparation of, 1, 99.
**Stilbene**, *di*- and *tri*-bromo-derivatives, bromo-*mono*- and -*di*-cyano-derivatives, 3.
**5-Styrylacridines**, 5, 344.
**5-Styrylacridine**, 5-amino-derivatives and their derivatives, and 5-nitro-derivatives, 6.
3:5-*p*-*di*-amino- and -nitro-, 3:7:5-*p*-*tri*amino-, and their derivatives, 347.
**α-(β-Styrylacrylyl)tetronic acid**, 242.
**5-Styryl-7-methylacridine**, 3:5-*p*-amino- and -nitro-, and their derivatives, 347.
**2-Styryl-7-methyl-3-*n*-amylchromone**, 4-nitro-, 435.
**2-Styryl-7-methyl-3-*n*-butylchromone**, 4′-nitro-, 435.
**2-Styryl-7-methyl-3-*n*-propylchromone**, 4′-nitro-, 434.
**Sulphur**, physical constants of, 17.
**Sulphur** *di*oxide, heat of adsorption of, on sugar charcoal, 351.
**Sulphur organic compounds** :—
**Sulphuric acids**, esters, alkyl–oxygen fission in, 446.
**Surfaces**, fresh, properties of, 535.
**Surface tension**, measurement of, by vibrating-jet method, 535.

T.

**Taurine**, synthesis of, 4.
**1:2:3:4-Tetrahydro*iso*arsinoline**, 2-chloro-, 550.
**Tetrahydrocannabinol**, derivatives of, 286.
**α-(β-2-Tetrahydrofurylpropionyl)tetronic acid**, 242.
**1:2:3:4-Tetrahydrophenazine** *di*-*N*-oxide, 325.
**1:9-(2′:3′:4′:5′-Tetrahydrophenylene)carbazole**, and its derivatives, 659.
**5:6:7:8-Tetramethyl-1:2-benzanthraquinone**, 241.
**2-(2′:3′:4′:5′-Tetramethylbenzoyl)-1-naphthoic acid**, 240.
**3:3:3′:3′-Tetramethylbis-1:1′-*spiro*hydrindene**, 4:5:6:4′:5′:6′- and 5:6:7:5′:6′:7′-*hexa*hydroxy-, hexa-acetyl derivatives, 486, 487.
**2:2:3:3-Tetramethyl-α-hydrindone**, and nitro-, 429.
**2:2:5′:4″-Tetramethyl-3′:4′:5′:6′-tetrahydrodibenzopyran**, 6″-hydroxy-, 6″-*O*-dichlorophosphoryl derivative, 286.
**Tetramminopalladous** chloride, interchange of hydrogen in, with deuterium oxide, 367.
**Tetramminoplatinous** chloride, interchange of hydrogen in, with deuterium oxide, 367.
**2:2′:4:4′-Tetra-*p*-anisylazadipyrromethine**, 593.
**Tetra(benzenesulphonamidoethyl)ethylenediamine**, *tetra*-*p*-amino-, and its tetra-acetyl derivative, 609.
**Tetra(benzenesulphonamidomethyl)methane**, *tetra*-*p*-amino-, and its tetra-acetyl derivative, 608.
**2:2′:4:4′-Tetraphenylazadipyrromethine**, and its metallic complexes, 592, 597.
**Tetraphenylene**, and its bromo- and *tetra*nitro-derivatives, 326.
**2:2′:4:4′-Tetraphenyl-*meso*-phenyldipyrromethine**, and its copper complex, 597.
**2:2′:4:4′-Tetraphenyl-*meso*-phenyldipyrromethine**, 3:3-*di*amino-, dibenzoyl derivative, 599.
**Tetronic acid**, α-amino-, acetyl derivative, 242.
**Therapeutics**, quinoline series, 401, 404, 406, 413, 417, 419.
**Thiazinocyanines**, 243, 487.
**8-2′-Thiazylquinoline**, 420.
**Thiobenzophenone**, photo-oxidation of, 275.
**2-Thio-3-ethyltetrahydro-1:3-thiazine**, 247.
**Thioketones**, photo-oxidation of, in sunlight, 275.
**2-Thio-3-methyltetrahydro-1:3-thiazine**, 247.
**2-Thiotetrahydro-1:3-thiazine**, 246.
**Thiourea**, compound of, with lead nitrate, 661.
**Tilden Lecture**, 629.
**Tolane**, 4:4′-*di*cyano-, 3.
**Toluene**, 2-nitro-5-hydroxy-, 5-benzyl derivative, 49.
**6-*p*-Tolueneazo-2:4-bis*di*chloromethylene-1:3-benzdioxin**, 321.
**4-*p*-Tolueneazonaphthalene-1-azoresorcinol**, 6-nitro-, 393.
**4-*p*-Tolueneazo-1-naphthylamine**, 6-nitro-, and its acetyl derivative, 393.
***p*-Toluenesulphon-2-naphthalide**, 1-bromo-6-nitro-, 392.
6-nitro-, 391.
2:4:6-*tri*nitro-, 393.
***m*-Toluidine** hydrochloride, action of methyl alcohol on, 14.
***m*-Toluidine-6-sulphonamide**, and *mono*- and *di*-bromo-, 78.
***o*-Tolyl** carbonate, 500.
ethers, 4-nitro-, 432.
methyl ether, 5-nitroso-, 223.
***m*-Tolyl** methyl ether, 6-nitroso-, 223.
**β-*p*-Tolyl-ααββ-tetramethylpropionic acid.** See β-*p*-Tolyl-ααβ-trimethyl-*n*-butyric acid.
**β-*p*-Tolyl-ααβ-trimethyl-*n*-butyric acid**, 428.
**4-Triacetyl-*d*-xylosidamino-2-methylthiopyrimidine**, 6-amino-, acetyl derivative, 573.
**Trialkyl** *ortho*phosphates, physical constants of, 23.
**Tri-(β-benzenesulphonamidoethyl)amine**, *tri*-β-*p*-amino-, and its triacetyl derivative, 608.
**αβγ-Tri(benzenesulphonamido)propane**, αβγ-*tri*-*p*-amino-, and its triacetyl derivative, 608.
**Trideuterammonia**, compounds of, with metallic salts, 104.
**Triketohydrindene**, 71.
**Trimethin[2-(3-ethyldihydrobenzbenzoxazole)][2-(*peri*naphtha-1:3-thiazines)]**, 490.
**Trimethin[2-(3-ethyldihydrobenzbenzthiazole)][2-(*peri*naphtha-1:3-thiazines)]**, 490.
**Trimethin[2-(3-ethyldihydrobenzoxazole)][2-(*peri*naphtha-1:3-thiazine)]**, and its hydrochloride, 490.
**Trimethin[2-(3-ethyldihydrobenzthiazole)][2-*peri*naphtha-1:3-thiazine)]**, 490.
**Trimethylbenzoyl-2-methylnaphthalenes**, 240.
**Trimethylbenzoylnaphthoic acids**, and their derivatives, 240.
**2:3:7-Trimethylchromone**, 434.
**2:6:11-Trimethyl-*n*-tridecane**, 267.
**2:2:5′-Trimethyl-3′:4′5:′6′-tetrahydrodibenzopyran**, 6″:4″-*di*-hydroxy-, alkyl derivatives, 286.
**2:2′:4-Triphenyl-4′-*p*-anisylazadipyrromethine**, 595.
**2:2′:4-Triphenyl-4′-*p*-anisyldipyrromethine**, 597.
**Triterpene group**, 477.
**Triterpene resinols.** See under Resinols.
**Triuret**, properties of, 603.
**Tutin**, and its acetyl derivative, and α- and β-bromo-, 50.
hydrogenation of, 143.

U.

***sec.*-Undecyl-*n*-dodecylmalonic acid**, ethyl ester, 618.
**Unsaturation**, tests for, in polycyclic hydroaromatic compounds, 482.
**Urea**, properties of, 603.

V.

**Velocity of reaction** in solution, 629.
**Volume**, molecular, constitution and, 146.

W.

**Widman–Stoermer reaction**, effect of substitution on, 447.

X.

**4-*d*-Xylosidamino-2-methylpyrimidine**, 6-amino-, 573.
**4-*d*-Xylosidamino-2-methylthiopyrimidine**, 6-amino-, and its 6-acetyl derivative, 572.

Y.

**Yeast ribonucleic acid**, constitution of, 625.
**Ytterbium**, separation of, 8.

Z.

**Zinc** bromide, activity coefficient of, 157.
chloride, activity coefficient of, 157.
iodide, activity coefficient of, 157.

# FORMULA INDEX.

THE following index of organic compounds of known empirical formula is arranged according to Richter's system (see *Lexikon der Kohlenstoff-Verbindungen*).

The elements are given in the order, C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

The compounds are arranged—

Firstly, in groups according to the number of carbon atoms (thus $C_1$ group, $C_2$ group, etc.).

Secondly, according to the number of other elements besides carbon contained in the molecule (thus 5 IV indicates that the molecule contains five carbon atoms and four other elements).

Thirdly, according to the nature of the elements present in the molecule (given in the above order).

Fourthly, according to the number of atoms of each single element (except carbon) present in the molecule.

Salts are placed with the compounds from which they are derived. The chlorides, bromides, iodides, and cyanides of quaternary ammonium bases, however, are registered as group-substances.

## $C_1$ Group.


**$CH_2O$** Formaldehyde, electrolytic reduction of, 90.
**$CH_2O_2$** Formic acid, catalytic reduction by, 84, 281.
**$CNCu$** Cuprous cyanide, 79.

**1 III**

**$CH_4ON_2$** Urea, properties of, 603.


## $C_2$ Group.


**$C_2H_2O_4$** Oxalic acid, rare-earth salts, 40.
**$C_2H_4O$** Acetaldehyde, condensation products of, 42.
**$C_2H_5Cl$** Ethyl chloride, heat of adsorption of, on sugar charcoal, 351.
**$C_2H_6O$** Methyl ether, free energy of, 589.

**2 III**

**$C_2H_3O_2Cl$** Chloroacetic acid, sodium salt, elimination of chlorine from, 517.
**$C_2H_5O_2N_3$** Biuret, properties of, 603.

**2 IV**

**$C_2H_7O_3NS$** Taurine, synthesis of, 4.
**$C_2H_7O_4NS$** β-Aminoethyl hydrogen sulphate, 4.


## $C_3$ Group.


**$C_3H_6N_4$** Malondiamidine, dihydrochloride of, 575.

**3 III**

**$C_3H_3O_2N$** Cyanoacetic acid, dissociation constant of, 516.
**$C_3H_3O_3N_3$** Cyanuric acid, calcium salt, tetrahydrate, 606.
**$C_3H_5O_3N_4$** Triuret, properties of, 605.


## $C_4$ Group.


**$C_4H_2O_3$** Maleic anhydride, reaction of, with anthranil, 654.
**$C_4H_6O$** Crotonaldehyde, oxygen absorption by, in presence of catalysts, 463.
Methyl vinyl ketone, preparation and polymerisation of, 25.
**$C_4H_6O_2$** Methacrylic acid, synthesis of, 238.
**$C_4H_6N_4$** 4:6-Diaminopyrimidine, 575.
**$C_4H_7N_5$** 4:5:6-Triaminopyrimidine, 387.
**$C_4H_8O_2$** Aldol, polymerisation of, 445.
3-Ketobutanol, 29.
**$C_4H_9Br$** *n*-Butyl bromide, reaction of, with hydroxylic solvents, 255.

**4 III**

**$C_4H_2N_2Cl_2$** 4:6-Dichloropyrimidine, 575.
**$C_4H_4O_2N_2$** 4:6-Dihydroxypyrimidine, 389.
**$C_4H_5O_2N$** β-Cyanopropionic acid, preparation of, and its dissociation constant, 516.
**$C_4H_8ON_2$** *l*-3-Aminopyrrolidone, and its salts, 40.


## $C_5$ Group.


**$C_5H_4N_4$** 4-Amino-5-cyanopyrimidine, and its picrate, 387.
**$C_5H_5N_5$** Adenine, synthesis of, 386.
**$C_5H_8N_4$** 4:6-Diamino-2-methylpyrimidine, and its picrate, 385.
**$C_5H_9Cl$** αγ-Dimethylallyl chloride, 349.

### 5 III

$C_5H_4N_2Cl_2$ 4:6-Dichloro-2-methylpyrimidine, 385.
$C_5H_7O_2N$ γ-Cyano-*n*-butyric acid, preparation of, and its dissociation constant, 516.
Dimethylcyanoacetic acid, preparation of, and its dissociation constant, 516.
$C_5H_7N_5S$ 4:6-Diamino-5-thioformamidopyrimidine, 387.
$C_5H_8N_4S$ 4:6-Diamino-2-methylthiopyrimidine, and its picrate, 573.
$C_5H_9NS$ 2-Methylthiodihydro-1:3-thiazine, 246.
$C_5H_9NS_2$ 2-Thio-3-methyltetrahydro-1:3-thiazine, 246.
$C_5H_9N_5S$ 4:5:6-Triamino-2-methylthiopyrimidine, 385.
$C_5H_{11}O_2N$ α-Acetamido-γ-hydroxypropane, 247.
$C_5H_{11}O_3N$ *dl*-*N*-β-Hydroxypropylglycine, 376.

## $C_6$ Group.

$C_6H_4O_2$ Benzoquinone, tautomerism of, in systems with *p*-nitrosophenol, 89.
$C_6H_6O$ Phenol, ultra-violet absorption spectrum of, 380.
$C_6H_7N_5$ 2-Methyladenine, and its picrate, 385.
$C_6H_8O$ Hex-3-en-5-yn-2-ol, 263.

### 6 III

$C_6H_3O_6N_3$ *s*-Trinitrobenzene, compound of, with *p*-iodoaniline, 153; molecular compounds of, with unsaturated ketones, 462.
$C_6H_4N_2Cl_4$ 2:3:5:6-Tetrachloro-1:4-diaminobenzene, 234.
$C_6H_5N_6Fe$ Hydroferrocyanic acid, potassium and sodium salts, colour variation in, 223.
$C_6H_5O_2N$ *p*-Nitrosophenol, tautomerism of, in systems with benzoquinone, 89.
$C_6H_5N_5S$ 2-Methylthioadenine, 385.
$C_6H_6NI$ *p*-Iodoaniline, compound of, with *s*-trinitrobenzene, 153.
$C_6H_7O_4N$ α-Acetamidotetronic acid, 242.
$C_6H_9N_5S$ 4:6-Diamino-5-thioformamido-2-methylpyrimidine, 385.
$C_6H_9N_5S_2$ 4:6-Diamino-5-thioformamido-2-methylthiopyrimidine, 385.
$C_6H_{10}O_2N_2$ 3-Acetamidopyrrolidone, 40.
$C_6H_{10}N_4S$ 6-Amino-4-methylamino-2-methylthiopyrimidine, 385.
$C_6H_{11}NS_2$ 2-Ethylthiodihydro-1:3-thiazine, 246.
2-Thio-3-ethyltetrahydro-1:3-thiazine, 247.
$C_6H_{12}ON_2$ *dl*-3-Aminohomopiperidone, and its salts, 39.
$C_6H_{13}O_2N$ *N*-β-Hydroxy*iso*butylglycine, 377.
β-Hydroxypropylalanine, 378.
$C_6ON_2Cl_4$ 2:3:5:6-Tetrachlorobenzene-4-diazo-1-oxide, 235.

### 6 IV

$C_6HON_2Cl_3$ 3:4:6-Trichlorobenzene-2-diazo-1-oxide, 237.
$C_6HO_3NCl_4$ 2:3:5:6-Tetrachloro-4-nitrophenol, 235.
$C_6HO_4N_2Cl_4$ 2:3:5:6-Tetrachloro-4-nitro-*N*-nitroaniline, 373.
$C_6H_2O_2N_2Cl_4$ 2:3:5:6-Tetrachloro-4-nitroaniline, 234.
2:3:5:6-Tetrachloro-*N*-nitroaniline, 373.
$C_6H_4O_2NF$ 3-Fluoro-4-nitrosophenol, absorption spectrum of, 89.
$C_6H_5O_2N_2Cl_3$ 3:5-Dichloro-1-nitro-2:6-diaminobenzene, 576.
$C_6H_6O_2N_4Cl_2$ 3:5-Dichloro-1-nitro-2:4:6-triaminobenzene, 577.
$C_6H_6O_3N_2S$ Benzenediazosulphonic acids, isomeric, potassium salts, structure of, 470.
$C_6H_6ON_4S$ 4-Amino-5-thioformamido-6-hydroxy-2-methylpyrimidine, 384.
$C_6H_6O_3N_2S$ *p*-Hydroxylaminobenzenesulphonamide, complex formation and rearrangement of, 656.
$C_6H_{12}NIS_2$ 2-Methylthiodihydro-1:3-thiazine methiodide, 246.

### 6 V

$C_6H_{24}O_6N_{14}S_2Pb$ Lead nitrate–thiourea, 661.
$C_6H_{24}O_{18}N_{12}Cl_3Ga$ Hexaureagallium perchlorate, 77.

## $C_7$ Group.

$C_7H_{12}$ 1-Methyl*cyclo*hexene, 475.

### 7 II

$C_7H_6O_2$ Benzoic acid, dissociation constants of, 271.
$C_7H_8O_2$ *o*-Hydroxybenzyl alcohol, 475.
$C_7H_9N$ *m*-Toluidine, hydrochloride of, action of methyl alcohol on, 14.
$C_7H_{10}O$ 2- and 3-Methylhex-3-en-5-yn-2-ols, 263.

### 7 III

$C_7H_3O_3Cl_3$ 2:3:5-Trichloro-6-nitro-*p*-benzoquinone, 236.
$C_7H_5ON$ Anthranil, reaction of, with maleic anhydride, 654.
$C_7H_4ON_4$ Acetylformamidinomethylenemalononitrile, 387.
$C_7H_4OBr_2$ Dibromo-*p*-cresols, 526.
$C_7H_6ON_4$ 2-Hydroxy-6:9-dimethylpurine, 385.
$C_7H_7N_5S$ 2-Methylthio-9-methyladenine, 386.
$C_7H_{11}N_5S_2$ 6-Amino-4-methylamino-5-thioformamido-2-methylthiopyrimidine, 385.
$C_7H_{14}O_2N_2$ Malondi-iminoether, dihydrochloride of, 575.

### 7 IV

$C_7H_3O_4N_3Cl_4$ 2:3:5:6-Tetrachloro-4-nitro-*N*-nitromethylaniline, 373.
$C_7H_4O_2N_2Cl_4$ 2:3:5:6-Tetrachloro-*N*-nitromethylaniline, 373.
$C_7H_4O_3NCl_3$ 3:4:6-Trichloro-2-nitroanisole, 236.
$C_7H_4O_5N_2Cl_2$ 2:3:5-Trichloro-4-nitro-6-methoxy-*N*-nitroaniline, 236.
$C_7H_5ONCl_4$ 3:4:5:6-Tetrachloro-*o*-anisidine, 237.
$C_7H_5OClBr_2$ 3-Chloro-2:5-dibromo-*p*-cresol, 527.
$C_7H_5O_3N_2Cl_3$ 3:4:6-Trichloro-5-nitro-*o*-anisidine, 236.
$C_7H_6ONCl_3$ 3:4:6-Trichloro-*o*-anisidine, 236.
$C_7H_7ON_2Cl_3$ 3:4:6-Trichloro-2:5-diaminoanisole, 237.
$C_7H_8ON_4S$ 6-Hydroxy-2-methylthio-9-methylpurine, 386.
$C_7H_{10}ON_4S$ 4-Methylamino-5-thioformamido-2-hydroxy-6-methylpyrimidine, 385.
$C_7H_{10}O_2N_2S$ *m*-Toluidine-6-sulphonamide, 78.

### 7 V

$C_7H_3ONCl_3Br$ 3:4:6-Trichloro-5-bromo-*o*-anisidine, 237.
$C_7H_6O_2N_2Br_2S$ Dibromo-*m*-toluidine-6-sulphonamide, 79.
$C_7H_7O_2N_2BrS$ Bromo-*m*-toluidine-6-sulphonamide, 78.

## $C_8$ Group.

$C_8H_8O_3$ Mandelic acid, effect of heat on, 249.
Mandelic acids, solubilities of, in water, 231.
$C_8H_{10}O_2$ Acetylhex-3-en-5-yn-2-ol, 263.
$C_8H_{10}N_2$ 1:2-Dicyano*cyclo*hexane, 517.
$C_8H_{12}O_4$ Crotyl crotonate, 467.
$C_8H_{16}O_6$ Methyl β-methylgalactosides, 53.

### 8 III

$C_8H_5ON_3$ β-(α-Furyl)-β-aminomethylenemalononitrile, 390.
$C_8H_6O_2N_2$ Quinoxaline di-*N*-oxide, 324.
$C_8H_6O_2N_2$ 4:6-Dihydroxy-2-α-furylpyrimidine, 389.
$C_8H_7ON$ 5-Hydroxyindole, 49.
$C_8H_7O_2Cl$ Phenylchloroacetic acid, sodium salt, hydrolysis of, 80.
$C_8H_7O_2Br$ Phenylbromoacetic acid, sodium salt, hydrolysis of, 80.
$C_8H_8OBr_2$ Dibromo-4-ethylphenols, 527.
$C_8H_9O_2N$ 5-Nitroso-*o*-tolyl methyl ether, 223.
6-Nitroso-*m*-tolyl methyl ether, 223.
$C_8H_{10}O_2N_4$ 1-Nitrophenyl-3:3-dimethyltriazens, 443.
$C_8H_{10}O_2Cl_2$ *trans*-Hexahydrophthaloyl chloride, 517.
$C_8H_{10}O_4N_4$ 2:4-Dinitro-β-aminoethylaniline, and its hydrochloride, 556.
$C_8H_{10}NCl$ *p*-Chloro-*N*-ethylaniline, 65.
$C_8H_{11}O_2N$ *trans*-1-Cyano*cyclo*hexane-2-carboxylic acid, 517.
$C_8H_{14}O_2N_2$ *dl*-3-Acetamidohomopiperidone, 40.
$C_8H_{15}O_3N$ Rosmarinecine, 454.

### 8 IV

$C_8H_4O_3N_2Cl_4$ Acetyl-2:3:5:6-tetrachloro-4-nitroaniline, 234.
2:3:5:6-Tetrachloro-*N*-nitroacetanilide, 372.
$C_8H_5ONCl_4$ Acetyltetrachloroaniline, 233.
$C_8H_5O_2N_2Cl$ 6-Chlorophthalaz-1:4-dione, 659.
$C_8H_6ON_2Cl_4$ 2:3:5:6-Tetrachloroaminoacetamidobenzene, 234.
$C_8H_8O_6N_2S$ *N*-*m*-Nitrobenzenesulphonylglycine, 378.
$C_8H_9ON_2Cl$ *p*-Chlorophenyl-*N*-ethylnitrosoamine, 67.
$C_8H_{11}O_3NS$ *m*-Cresol-6-sulphonamide, 79.
$C_8H_{16}NIS_2$ 2-Ethylthiodihydro-1:3-thiazine ethiodide, 246.

## $C_9$ Group.

$C_9H_4O_3$ Triketohydrindene, 71.
$C_9H_9Cl$ à-Chloro-α-benzylethylene, 69.
$C_9H_{10}Br_2$ *o*-β-Bromoethylbenzyl bromide, syntheses with, 547, 550.
$C_9H_{14}O_3$ 1:3-Dioxanyl-5-*iso*butenyl ketone, 30.

### 9 III

$C_9H_6O_4N_2$ α-2:4-Dinitrophenylallene, 70.
$C_9H_6NCl$ 5-Chloroquinoline, and its picrate, 444.
$C_9H_7O_3N$ α-*p*-Nitrophenylallylene, 70.
$C_9H_7O_3N$ 5-Hydroxyindole-2-carboxylic acid, 49.
$C_9H_8O_2N_2$ 2-Methylquinoxaline di-*N*-oxide, 324.
$C_9H_{10}ClAs$ 2-Chloro-1:2:3:4-tetrahydro*iso*arsinoline, 550.
$C_9H_{11}O_2N_3$ 1-*o*-Carboxyphenyl-3:3-dimethyltriazen, 443.
$C_9H_{12}O_2N_4$ 4-Methoxy-2-methylbenzenediazoaminocarbonamide, 223.
$C_9H_{12}O_4S$ 3-Ethoxytoluene-6-sulphonic acid, salts, 168.
$C_9H_{13}O_2N$ *cyclo*Hexylcyanoacetic acid, preparation of, and its dissociation constant, 216.
$C_9H_{13}O_3N$ Adrenaline, oxidation of, 48.
$C_9H_{17}ON$ 1-Methyl*cyclo*hexane-1-acetamide, 502.
$C_9H_{17}O_2Cl$ Ethyl β-chloro-αα-trimethyl-*n*-butyrate, 429.

### 9 IV

$C_9H_7O_4N_3Cl$ β-Chloro-α-2:4-dinitrophenyl-$\Delta^{\alpha}$-propylene, 70.
$C_9H_7O_4N_2Cl_3$ Acetyl-3:4:6-trichloro-5-nitro-*o*-anisidine, 236.
$C_9H_8O_3NCl$ β-Chloro-α-*p*-nitrophenyl-$\Delta^{\alpha}$-propylene, 70.
$C_9H_8O_2NCl_3$ Acetyl-3:4:6-trichloro-*o*-anisidine, 236.
$C_9H_8O_4N_2S$ 5-Acetamido-*o*-benzoicsulphinide, 79.
$C_9H_9O_2N_2Cl_3$ 3:4:6-Trichloro-2-acetamido-5-aminoanisole, 237.
$C_9H_{10}O_3NCl$ 4-Chloro-2-nitro-3:5-dimethylphenyl methyl ether, 445.
$C_9H_{10}O_5N_2S$ 2:4-Dinitro-3-ethoxytoluene-6-sulphonic acid, salts, 169.
$C_9H_{11}O_3ClS$ 3-Ethoxytoluene-6-sulphonyl chloride, 168.
$C_9H_{11}O_3NS$ 4-Nitro-3-ethoxytoluene-6-sulphonic acid, salts, 169.
$C_9H_{12}O_3N_2S$ Aceto-*m*-toluidide-6-sulphonamide, 78.
$C_9H_{15}O_3NI$ Rosmarinecine methiodide, 454.

### 9 V

$C_9H_7O_2NCl_3Br$ Acetyl-3:4:6-trichloro-5-bromo-*o*-anisidine, 237.
$C_9H_9O_7N_2ClS$ 2:4-Dinitro-3-ethoxytoluene-6-sulphonyl chloride, 169.
$C_9H_{10}O_3NClS$ 4-Nitro-3-ethoxytoluene-6-sulphonyl chloride, 169.
$C_9H_{11}O_3N_2BrS$ Bromoaceto-*m*-toluidide-6-sulphonamide, 78.

## $C_{10}$ Group.

$C_{10}H_{18}$ Dihydromyrcene, 476.

### 10 II

$C_{10}H_8N_2$ Quinolineamidines, and their salts, 420.
$C_{10}H_{10}O$ 1-*p*-Anisylprop-1-yne, 611.
$C_{10}H_{10}N_2$ 2:3-Dimethylquinoxaline, Diels–Alder synthesis with, 651.
$C_{10}H_{10}N_6$ 4:6-Diamino-5-benzeneazopyrimidine, 387.
$C_{10}H_{11}Cl$ β-Chloro-α-phenyl-$\Delta^{\alpha}$-butylene, 69.
$C_{10}H_{12}O_3$ 4-Ethoxy-*m*-toluic acid, 320.
*iso*Propoxybenzoic acid, 432.
$C_{10}H_{12}N_4$ 1:3:5:7-Tetra-aminonaphthalene, 36.
$C_{10}H_{12}As$ 2-Methyl-1:2:3:4-tetrahydro*iso*arsinoline, 549.
$C_{10}H_{14}O$ 7-Methylnonadienynols, 267.
$C_{10}H_{14}O_2$ Decadien-5-yndiols, 269.
$C_{10}H_{14}O_4$ Ethylene dimethacrylate, 239.
$C_{10}H_{15}N$ 2:4-Dimethyl-*N*-ethylaniline, 65.
$C_{10}H_{16}O$ Decenynols, 265.
5-Ethyloct-5-en-7-yn-4-ol, 264.
7-Methylnon-7-en-5-yn-4-ol, 267.
$C_{10}H_{16}O_5$ Senecic acid, 454.
$C_{10}H_{16}Cl_2$ Dichlorodihydromyrcene, 296.
$C_{10}H_{17}Cl$ Chlorodihydromyrcene, 296.
$C_{10}H_{18}O_2$ *n*-Hexyl methacrylate, 239.
$C_{10}H_{20}O$ 7-Methylnonanones, 267.
$C_{10}H_{22}O$ 7-Methylnonanols, 267.
$C_{10}H_{22}O_2$ Decane-2:9-diol, 269.

### 10 III

$C_{10}H_4O_8N_4$ Tetranitronaphthalenes, 33.
$C_{10}H_6O_4N_2$ 1:3-Dinitronaphthalene, preparation of, 433.
1:6-Dinitronaphthalene, preparation of, 86.
Dinitronaphthalenes, monoreduction of, 318.
$C_{10}H_5O_6N_4$ 2:4:6-Trinitro-1-naphthylamine, 393.
$C_{10}H_7ON$ Quinolinealdehydes, 415.
$C_{10}H_7OCl$ 4-Chloro-2-naphthol, 469.
$C_{10}H_7OI$ 4-Iodo-2-naphthol, 469.
$C_{10}H_7O_4N_3$ 2:3-Dinitro-1-naphthylamine, 635.
Dinitro-1-naphthylamines, 393.
$C_{10}H_8O_2N_2$ 3-Nitro-2-naphthylamine, and its picrate, 636.
6-Nitro-1-naphthylamine, halogenation, nitration, mercuration, and diazo-coupling of, 391.
$C_{10}H_8N_2S$ Quinolinethioamides, 419.
$C_{10}H_9ON_3$ Quinolinecarboxyhydrazides, 415.
$C_{10}H_9O_3N$ Methyl 5-hydroxyindole-2-carboxylate, 49.
$C_{10}H_{10}O_4N_4$ 1-Phenyl-3:3-dimethyltriazen-3':4'-dicarboxyimide, 444.
$C_{10}H_{11}OCl$ Chloro-α-*p*-anisyl-$\Delta^{\alpha}$-propylenes, 611.
$C_{10}H_{11}OBr$ β-Bromo-α-*p*-anisyl-$\Delta^{\alpha}$-propylene, 611.
$C_{10}H_{11}O_2Cl$ 6-Chloro-4-methoxy-3-methylacetophenone, 500.
$C_{10}H_{11}O_3N$ 5-Nitro-4-ethoxy-*m*-toluic acid, 320.
$C_{10}H_{13}O_2N$ Ethyl 1-cyano*cyclo*hexane-2-carboxylate, 516.
β-3:4-Methylenedioxyphenyl*iso*propylamine, preparation of, 15.
$C_{10}H_{12}O_2N_2$ 1-*o*-Carbomethoxyphenyl-3:3-dimethyltriazen, 443.
$C_{10}H_{13}O_3N$ 4-Nitro-*o*-tolyl *n*-propyl ether, 432.
$C_{10}H_{13}Cl_2As$ 2-Methyl-1:2:3:4-tetrahydro*iso*arsinoline dichloride, 550.
$C_{10}H_{14}O_2N_2$ β-Hydroxypropylphenylcarbamide, 377.
$C_{11}H_{14}O_4N_2$ *d*-Ribobenziminazole, 628.
$C_{10}H_{15}O_3N$ Ethyl *cyclo*hexanone-2-carboxylate cyanohydrin, 516.
$C_{10}H_{16}O_4N_4$ 6-Amino-4-*d*-xylosidamino-2-methylpyrimidine, 574.
$C_{10}H_{17}O_2N$ 1-Methyl*cyclo*hexane-1-malonamic acid, 502.
$C_{10}H_{20}O_2N_2$ Decane-2:9-dione dioxime, 269.

### 10 IV

$C_{10}H_5ON_2Cl$ 4-Chloronaphthalene-1:2-diazo-oxide, 322.
$C_{10}H_5ON_2I$ 4-Iodonaphthalene-1:2-diazo-oxide, 322.
$C_{10}H_5O_2NBr_2$ 1:2- and 1:4-Dibromo-6-nitronaphthalenes, 392.
$C_{10}H_6O_2NCl$ 1-Chloro-6-nitronaphthalene, 392.
$C_{10}H_6O_2NBr$ 1-Bromo-6- and -7-nitronaphthalenes, 392.
$C_{10}H_6O_2NI$ 1-Iodo-6-nitronaphthalene, 392.
$C_{10}H_6O_2N_2Cl_2$ 2:4-Dichloro-6-nitro-1-naphthylamine, 392.
$C_{10}H_6O_2N_2Br_2$ 2:4-Dibromo-6-nitro-1-naphthylamine, 392.
$C_{10}H_6O_4N_2Cl_4$ Diacetyl-2:3:5:6-tetrachloro-4-nitroaniline, 234.
$C_{10}H_7O_2NCl_4$ Diacetyltetrachloroaniline, 233.
$C_{10}H_7O_2N_2Br$ 4-Bromo-6-nitro-1-naphthylamine, 392.
$C_{10}H_7O_2N_2I$ 4-Iodo-6-nitro-1-naphthylamine, 393.
$C_{10}H_8O_2N_2Cl_4$ 2:3:5:6-Tetrachloro-4-aminodiacetanilide, 234.
$C_{10}H_9O_4N_2Cl_2$ 3:5-Dichloro-1-nitro-2:6-diacetamidobenzene, 576.
$C_{10}H_{12}O_2N_2Br$ 2-Bromo-4-methoxyacetophenone semicarbazone, 526.
$C_{10}H_{12}O_2NCl$ 4-Chloro-2-nitro-3:5-dimethylphenyl ethyl ether, 445.
$C_{10}H_{12}O_5N_2S$ 4-Nitrobenzenesulphonylacetimino-ether, 103.
$C_{10}H_{12}O_6N_2S$ *N*-*m*-Nitrobenzenesulphonylglycine, ethyl ester, 378.
$C_{10}H_{13}O_4NS$ Phenylacetamidoethanesulphonic acid, sodium salt, 5.
$C_{10}H_{14}O_2NCl$ Ethyl 1-chloro-1-cyano*cyclo*hexane-2-carboxylate, 517.
$C_{10}H_{15}O_4N_3S$ γ-Amino-α-(*p*-aminobenzenesulphonamido)-*n*-butyric acid, 40.
$C_{10}H_{16}O_4N_4S$ 6-Amino-4-*d*-xylosidamino-2-methylthiopyrimidine, 572.

### 10 V

$C_{10}H_5O_2NBrI$ Bromoiodo-6-nitronaphthalenes, 393.

## $C_{11}$ Group.

$C_{11}H_6O_3$ α-(β-2-Furylacrylyl)tetronic acid, 242.
$C_{11}H_{10}O_2$ 2:7-Dimethylchromone, 434.
$C_{11}H_{10}N_2$ *o*-Aminophenylpyridines, and their picrates, 317.
$C_{11}H_{11}N_3$ α-3:4-Diaminophenylpyridine, 405.
β-3:4-Diaminophenylpyridine, 413.
$C_{11}H_{12}O_4$ Propionylmandelic acids, 228.
$C_{11}H_{13}Cl$ β-Chloro-α-phenyl-$\Delta^{\alpha}$-amylene, 69.
$C_{11}H_{14}O$ 6-Hydroxy-5-methyltetralin, 493.
$C_{11}H_{14}O_3$ *n*-Butoxybenzoic acid, 432.
$C_{11}H_{18}O$ 6-Methylcarvomenthone, 502.

### 11 III

$C_{11}H_4O_3Cl_6$ 5:7-Dichloro-6-methoxy-2:4-bisdichloromethylene-1:3-benzdioxin, 320.
$C_{11}H_6O_3Cl_6$ 5:7-Dichloro-6-methoxy-2:4-bistrichloromethyl-1:3-benzdioxin, 320.
$C_{11}H_7O_3Cl$ 7-Chloro-4-hydroxy-2-naphthoic acid, 12.
$C_{11}H_8O_3N_2$ 6-Nitroformo-1-naphthalide, 391.
α-3-Nitro-4-hydroxyphenylpyridine, 412.
$C_{11}H_9ON$ γ-3-Hydroxyphenylpyridine, 411.
$C_{11}H_9OCl$ 4-Chloro-2-naphthyl methyl ether, 469.
$C_{11}H_9OBr$ 4-Bromo-2-naphthyl methyl ether, 469.
$C_{11}H_9OI$ 4-Iodo-2-naphthyl methyl ether, 469.
$C_{11}H_9O_2N_3$ α-3-Nitro-4-aminophenylpyridine, 405.
$C_{11}H_9O_2I$ 4-Iodo-2-naphthyl acetate, 469.
$C_{11}H_9O_3N_3$ β-3-Nitro-4-aminophenylpyridine, 413.
$C_{11}H_9O_3Cl$ 3-Chlorobenzylsuccinic anhydride, 12.
$C_{11}H_9O_3Br$ 3-Bromo-4-keto-1:2:3:4-tetrahydro-2-naphthoic acid, 12.
$C_{11}H_{10}ON_2$ α-3-Amino-4-hydroxyphenylpyridine, 412.
$C_{11}H_{11}O_4Cl$ 3-Chlorobenzylsuccinic acid, 12.
$C_{11}H_{11}O_6N_3$ Crotyl-3:5-dinitrophenylurethane, 467.
$C_{11}H_{13}O_3N$ β-Ethoxy-α-*p*-nitrophenyl-$\Delta^{\alpha}$-propylene, 70.
$C_{11}H_{16}IAs$ 2-Methyl-1:2:3:4-tetrahydro*iso*arsinoline methiodide, 549.
$C_{11}H_{23}ON_3$ 7-Methylnonan-2-one semicarbazone, 267.

### 11 IV

$C_{11}H_5O_4NCl_4$ 7-Nitro-6-methyl-2:4-bisdichloromethylene-1:3-benzdioxin, 320.
$C_{11}H_7O_2NCl_4$ 8-Amino-6-methyl-2:4-bisdichloromethylene-1:3-benzdioxin, 320.
$C_{11}H_7O_4NCl_6$ Nitro-6-methyl-2:4-bistrichloromethyl-1:3-benzdioxins, 320.
$C_{11}H_8O_3ClBr$ 7-Chloro-3-bromo-4-keto-1:2:3:4-tetrahydro-2-naphthoic acid, 12.
$C_{11}H_9O_2NCl_6$ 8-Amino-6-methyl-2:4-bistrichloromethyl-1:3-benzdioxin, 320.
$C_{11}H_9O_5N_2Cl_3$ Diacetyl-3:4:6-trichloro-5-nitro-*o*-anisidine, 236.
$C_{11}H_{10}O_3NCl_3$ Diacetyl-3:4:6-trichloro-*o*-anisidine, 236.
$C_{11}H_{11}O_3N_2Cl_3$ 2-Diacetyl-3:4:6-trichloro-5-amino-*o*-anisidine, 237.
3:4:6-Trichloro-2:5-diacetamidoanisole, 237.
$C_{11}H_{13}ON_2I$ 2-Keto-1:3-dimethyl-1:2-dihydroquinoxaline, 396.
$C_{11}H_{13}O_4NS$ *N*-Benzenesulphonyl-*N*-allylglycine, 376.
*N*-Benzenesulphonyl-6-methyl-2-morpholone, 376.
$C_{11}H_{13}O_5NS$ *N*-Benzenesulphonyl-*N*-acetonylglycine, 377.
$C_{11}H_{14}ON_2S_2$ 5:2′-(3′-Methyltetrahydrothiazolyl)ethylidene-3-ethylrhodanine, 249.
$C_{11}H_{14}O_3NCl$ 4-Chloro-2-nitro-3:5-dimethylphenyl *n*-propyl ether, 445.

$C_{11}H_{15}O_4NS$ Ethyl benzenesulphonyl-α-aminopropionate, 378.
Phenylpropionamidoethanesulphonic acid, sodium salt, 5.
$C_{11}H_{16}ON_2S_3$ 5:2′-(3′-Ethyltetrahydro-1′:3′-thiazyl)-3-ethylrhodanine, 249.
$C_{11}H_{15}O_5N_3S$ 6-Amino-4-*d*-mannosidamino-2-methylthiopyrimidine, 573.

### 11 V

$C_{11}H_{13}O_4NBr_2S$ *N*-Benzenesulphonyl-*N*-βγ-dibromopropylglycine, 378.

## $C_{12}$ Group.

$C_{12}H_8$ Diphenylene, 326.

### 12 II

$C_{12}H_{10}O_3$ 4-Hydroxy-1-methyl-2-naphthoic acid, 13.
4-Hydroxy-6-methyl-2-naphthoic acid, 12.
$C_{12}H_{10}O_4$ 4-Hydroxy-6-methoxy-2-naphthoic acid, 12.
$C_{12}H_{10}N_2$ 9-Aminocarbazole, and its picrate, 660.
$C_{12}H_{12}O$ 2:4-Dimethylnaphthol, 168.
$C_{12}H_{12}O_2$ γ-Phenyl-αα-dimethyl-Δβ-butyrolactone, 428.
$C_{12}H_{12}O_3$ 4-*tert.*-Butylphthalic anhydride, 145.
4-Keto-6-methyl-1:2:3:4-tetrahydro-2-naphthoic acid, 12.
4-Methylbenzylsuccinic anhydride, 12.
$C_{12}H_{12}O_4$ 4-Keto-6-methoxy-1:2:3:4-tetrahydro-2-naphthoic acid, 12.
4-Methoxybenzylsuccinic anhydride, 12.
$C_{12}H_{13}N_3$ 1-β-Naphthyl-3:3-dimethyltriazen, 444.
$C_{12}H_{14}O_2$ 6-Methoxy-5-methyl-1-tetralone, 493.
$C_{12}H_{14}O_3$ β-Benzoyl-α-methylbutyric acid, 428.
2-Methoxy-4-methylbenzoylacetone, 434.
$C_{12}H_{14}O_4$ 4-*tert.*-Butylphthalic acid, 145.
4-Methylbenzylsuccinic acid, 12.
$C_{12}H_{14}O_5$ 4-Methoxybenzylsuccinic acid, 12.
$C_{12}H_{16}O$ 6-Methoxy-5-methyltetralin, 493.
$C_{12}H_{16}O_2$ β-Phenyl-αα-dimethyl-*n*-butyric acid, 429.
$C_{12}H_{16}O_3$ *n*-Amyloxybenzoic acid, 432.
$C_{12}H_{20}O$ 2-Keto-9:10-dimethyldecalin, 502.

### 12 III

$C_{12}H_6O_9N_4$ Dinitrobenzeneazophenols, 380.
$C_{12}H_6N_2S$ 8-2′-Thiazylquinoline, 420.
$C_{12}H_9O_2Cl$ 4-Chloro-2-naphthyl acetate, 469.
$C_{12}H_9O_2Br$ 4-Bromo-2-naphthyl acetate, 469.
$C_{13}H_9NS$ 2-Methyl*peri*naphtha-1:3-thiazine, 489.
$C_{12}H_{10}O_2N_2$ *N*-Nitronitroso-1-naphthalide, 285.
$C_{12}H_{10}O_3N$ β-2-Nitro-5-methoxypyridine, 411.
$C_{12}H_{10}O_3N_2$ 3-Nitroaceto-2-naphthalide, 636.
α-Nitroaminophenyl-β-(2-furyl)ethylenes, 451.
Nitromethoxyphenylpyridines, and their picrates, 410.
$C_{12}H_{10}O_4N_2$ 2-Keto-1-methyl-1:2-dihydroquinoxaline-3-pyruvic acid, 400.
$C_{12}H_{11}O_2N$ Ethyl quinolinecarboxylates, 415.
$C_{12}H_{11}O_3Br$ 3-Bromo-4-keto-6-methyl-1:2:3:4-tetrahydro-2-naphthoic acid, 12.
$C_{12}H_{11}O_4Br$ 3-Bromo-4-keto-6-methoxy-1:2:3:4-tetrahydro-2-naphthoic acid, 12.
$C_{12}H_{12}ON_2$ Aminomethoxyphenylpyridines, 410.
$C_{12}H_{12}O_2N_2$ 1:2:3:4-Tetrahydrophenazine di-*N*-oxide, 325.
$C_{12}H_{13}O_5N$ *l*-Methylsuccinylanthranilic acid, 141.
$C_{12}H_{14}O_2Br_2$ Dibromo-6-hydroxy-2:4-diethylacetophenone, 274.
$C_{12}H_{15}O_2N$ αγ-Dimethylallyl phenylurethane, 351.
$C_{12}H_{15}O_2Br$ Bromo-6-hydroxy-3:4-diethylacetophenone, 274.
$C_{12}H_{15}O_4N_3$ Methyl 1-phenyl-3:3-dimethyltriazen-3′:4′-dicarboxylate, 444.
$C_{12}H_{19}O_2N$ Ethyl 1-methyl*cyclo*hexane-1-cyanoacetate, 502.

### 12 IV

$C_{12}H_6O_2N_2Cl_2$ 2:4-Dichloro-6-nitroaceto-1-naphthalide, 392.
$C_{12}H_{10}O_4N_2Hg$ 6-Nitro-1-naphthylamine-4-mercuriacetate, 393.
$C_{12}H_{13}O_6NS$ Acetylmandelamidoethanesulphonic acid, sodium salt, 5.
$C_{12}H_{15}O_4NS$ *N*-Benzenesulphonyl-*N*-allylalanine, 378.
*N*-Benzenesulphonyldimethyl-2-morpholones, 377.
*N*-Benzenesulphonyl-*N*-β-methylallylglycine, 377.
*N*-*p*-Toluenesulphonyl-*N*-allylglycine, 376.
*N*-*p*-Toluenesulphonyl-6-methyl-2-morpholone, 376.
$C_{12}H_{15}O_4N_2S$ 3-(*p*-Acetamidobenzenesulphonamido)pyrrolidone, 40.
$C_{13}H_{16}ON_2S_3$ 5:2′-(3′-Methyltetrahydro-1′:3′-thiazyl)ethylidene-3-ethylrhodanine, 249.
$C_{12}H_{17}O_4NS$ Ethyl *p*-toluenesulphonyl-α-aminopropionate, 378.
Mesitylenesulphonylalanine, 378.
$C_{12}H_{17}O_5NS$ *N*-*p*-Toluenesulphonyl-*N*-β-hydroxypropylglycine, 376.
$C_{12}H_{19}O_5N_3S$ 6-Acetamido-4-*d*-xylosidamino-2-methylthiopyrimidine, 573.
$C_{12}H_{19}O_4N_3S$ ε-Amino-α-(*p*-aminobenzenesulphonamido)-*n*-hexoic acid, 40.

### 12 V

$C_{13}H_{15}O_4NBr_2S$ *N*-Benzenesulphonyl-*N*-βγ-dibromopropylglycine, methyl ester, 378.
*N*-*p*-Toluenesulphonyl-*N*-βγ-dibromopropylglycine, 378.

## $C_{13}$ Group.

$C_{13}H_8N_2$ 6-β-Pyridylquinoxaline, 413.
$C_{13}H_{10}O_4$ α-(β-Phenylacrylyl)tetronic acid, 242.
$C_{13}H_{10}S$ Thiobenzophenone, photo-oxidation of, 275.
$C_{13}H_{11}N_3$ 3:5-Diaminoacridine, 461.
$C_{13}H_{12}O_3$ 4-Methoxy-1-methyl-2-naphthoic acid, 13.
Methyl 4-hydroxy-1-methyl-2-naphthoate, 13.
$C_{13}H_{12}O_4$ α-(β-Phenylpropionyl)tetronic acid, 242.
$C_{13}H_{13}N_3$ 8-γ-Cyanopropylaminoquinoline, 560.
$C_{13}H_{14}O$ 2-Methoxy-1:5-dimethylnaphthalene, 493.
$C_{13}H_{14}O_2$ γ-Phenyl-αaβ-trimethyl-$\Delta^{\beta}$-butyrolactone, 428.
$C_{13}H_{14}N_2$ 4-*p*-Aminophenyl-2:6-dimethylpyridine, 416.
$C_{13}H_{16}O$ 2-2:3:3-Tetramethyl-α-hydrindone, 429.
$C_{13}H_{16}O_2$ 6-Methoxy-2:5-dimethyl-1-tetralone, 494.
γ-Phenyl-αaβ-trimethylbutyrolactone, 428.
$C_{13}H_{16}O_3$ β-Benzoyl-aa-dimethyl-*n*-butyric acid, 428.
α-2-Methoxy-4-methylbenzoyl-α-methylactone, 434.
Methyl β-benzoyl-aa-dimethylpropionate, 428.
Methyl β-benzoyl-ββ-dimethylpropionate, 429.
Methyl β-benzoyl-α-methylbutyrate, 428.
$C_{13}H_{16}N_4$ 8-γ-Guanylpropylaminoquinoline, and its hydrochloride, 560.
$C_{13}H_{18}O_2$ Methyl β-phenyl-aa-dimethyl-*n*-butyrate, 429.
β-Phenyl-αaβ-trimethyl-*n*-butyric acid, 428.
$C_{13}H_{18}O_3$ *n*-Hexyloxybenzoic acid, 432.

### 13 III

$C_{13}H_9O_2N_3$ 4-Pyridylphthalimides, 444.
$C_{13}H_8O_2N_4$ 4-Amino-5-cyano-2:6-di-α-furylpyrimidine, 390.
$C_{13}H_9ON$ 4-Hydroxyacridine, 461.
$C_{13}H_9O_2N_3$ 3-Nitro-5-aminoacridine, and its hydrochloride, 461.
$C_{13}H_{10}O_2N_2$ 2-Nitrodiphenylamine-2′-aldehyde, 460.
$C_{13}H_{10}N_2S$ Methylthiazylquinolines, 419.
$C_{13}H_{11}OCl$ *m*-Chlorophenyl benzyl ether, 432.
$C_{13}H_{11}O_3N_3$ α-3-Nitro-4-acetamidophenylpyridine, 405.
$C_{13}H_{13}O_3N_4$ 4′-Nitro-4-hydroxy-2-methyldiazoaminobenzene, 223.
$C_{13}H_{13}O_2N$ Hex-3-en-5-yn-2-ol phenylurethane, 263.
$C_{13}H_{13}O_4N$ 5:6-Diacetoxy-1-methylindole, 48.
$C_{13}H_{15}O_3N$ Nitro-2:2:3:3-tetramethyl-α-hydrindone, 429.
$C_{13}H_{16}O_2N_2$ 8-γ-Hydroxypropylamino-6-methoxyquinoline, 561.
$C_{13}H_{17}ON_3$ 8-γ-Aminopropyl-γ-aminopropyl-6-methoxyquinoline, and its meconate, 557.
$C_{13}H_{17}O_4N$ β-Nitrophenyl-αaβ-trimethyl-*n*-butyric acid, 429.
$C_{13}H_{23}ON_3$ 2-Keto-9:10-dimethyldecalin semicarbazone, 502.

### 13 IV

$C_{13}H_9OCl_2Br$ 3:5-Dichlorophenyl *p*-bromobenzyl ether, 432.
$C_{13}H_9O_3NCl_4$ 8-Acetamido-6-methyl-2:4-bisdichloromethylene-1:3-benzdioxin, 320.
$C_{13}H_{10}O_3N_2S$ 4-Aminobenzenesulphonylbenzamidine, 103.
$C_{13}H_{10}O_2NF$ *m*-Fluorophenyl *o*-nitrobenzyl ether, 432.
$C_{13}H_{11}O_3NCl_6$ 8-Acetamido-6-methyl-2:4-bistrichloromethyl-1:3-benzdioxin, 320.
$C_{13}H_{11}O_4N_3S$ *N*-4-Nitrobenzenesulphonylbenzamidine, 103.
$C_{13}H_{12}O_2NI$ 2-Iodo-5:6-diacetoxy-1-methylindole, 48.
$C_{13}H_{15}ON_2Cl$ 8-γ-Chloropropylamino-6-methoxyquinoline, 562.
$C_{13}H_{16}O_4N_2S$ Ethyl *N*-*m*-nitrobenzenesulphonyl-*N*-allylaminoacetate, 378.
$C_{13}H_{17}O_4NS$ *N*-*p*-Toluenesulphonyl-6:6-dimethyl-2-morpholone, 377.
*N*-*p*-Toluenesulphonyl-*N*-β-methylallylglycine, 377.
$C_{13}H_{17}N_2IS$ 2-β-Anilinovinyldihydro-1:3-thiazine methiodide, 247.
$C_{13}H_{19}O_4NS$ Ethyl mesitylenesulphonamidoacetate, 377.
$C_{13}H_{20}O_5N_4S$ 6-Acetamido-4-*d*-mannosidamino-2-methylthiolpyrimidine, 573.
$C_{13}H_{21}N_2IS_2$ Bis-2-(3-methyldihydro-1:3-thiazine)trimethincyanine iodide, 249.

### 13 V

$C_{13}H_{16}O_6N_2Br_2S$ Ethyl *N*-*m*-nitrobenzenesulphonyl-*N*-allylaminoacetate dibromide, 378.
$C_{13}H_{17}O_4NBr_2S$ *N*-Benzenesulphonyl-*N*-βγ-dibromopropylglycine, ethyl ester, 378.

## $C_{14}$ Group.

$C_{14}H_{14}$ β-*tert*.-Butylnaphthalene, 144.

### 14 II

$C_{14}H_9Br_3$ 4:4′-α-Tribromostilbene, 3.
$C_{14}H_{10}O_3$ 2′:3′-Diketo-4-methoxy-1:2-*cyclo*pentenonaphthalene, 499.
$C_{14}H_{10}N_2$ Pyridylquinolines, and their salts, 403.
$C_{14}H_{10}Br_2$ Dibromostilbenes, 3.
$C_{14}H_{10}Br_4$ Tetrabromo-αβ-diphenylethanes, 2.
$C_{14}H_{11}N_3$ 8-Amino-6-α-pyridylquinoline, 405.
$C_{14}H_{12}O_3$ *m*-Benzyloxybenzoic acid, 432.
Furfurylidene-3-methoxyacetophenone, 499.
$C_{14}H_{12}O_5$ α-(β-*p*-Methoxyphenylacrylyl)tetronic acid, 242.

$C_{14}H_{13}N_3$ 5-Imino-10-methylacridane, 461.
5-Methylaminoacridine, 461.
$C_{14}H_{12}Br_2$ $a\beta$-Dibromo-$a\beta$-diphenylethane, 2.
$C_{14}H_{14}O_2$ 2-*tert.*-Butyl-1:4-naphthaquinone, 145.
$C_{14}H_{14}O_3$ Ethyl 4-hydroxy-1-methyl-2-naphthoate, 13.
Methyl 4-methoxy-1-methyl-2-naphthoate, 13.
$C_{14}H_{14}O_4$ 3-*m*-Methoxyphenyl-$\Delta^3$-*cyclo*penten-1-one-2-acetic acid, 499.
$C_{14}H_{16}O_2$ 2:7-Dimethyl-3-*n*-propylchromone, 434.
$C_{14}H_{16}O_4$ Methyl 6-methoxy-5-methyl-1-tetralone-2-carboxylate, 494.
$C_{14}H_{16}O_5$ 4:7-Diketo-*m*-methoxyphenylheptoic acid, 499.
$C_{14}H_{18}O$ 1-Keto-7-*tert.*-butyl-1:2:3:4-tetrahydronaphthalene, 145.
12-Methyl-1:2:3:4:12:13-hexahydroxanthen, 476.
$C_{14}H_{18}O_3$ $a$-2-Methoxy-4-methylbenzoyl-$a$-ethylacetone, 434.
Methyl $\beta$-benzoyl-$aa$-dimethyl-*n*-butyrate, 428.
Methyl $a\beta\beta$-trimethylpropionate, 429.
$C_{14}H_{18}O_4$ Deca-3:7-dien-5-yn-2:9-diol diacetate, 269.
$C_{14}H_{20}O_2$ Methyl $\beta$-phenyl-$a\beta\beta$-trimethyl-*n*-butyrate, 429.
$\beta$-*p*-Tolyl-$aa\beta$-trimethyl-*n*-butyric acid, 428.
$C_{14}H_{20}O_3$ *n*-Heptyloxybenzoic acid, 432.

### 14 III

$C_{14}H_6O_6N_2$ 2-Nitroacridone-7-carboxylic acid, 458.
$C_{14}H_9O_4N_3$ 8-Nitro-6-$a$-pyridylquinoline, 405.
$C_{14}H_{10}ON_2$ 8-Hydroxy-5-$a$-pyridylquinoline, 412.
$C_{14}H_{10}O_2N_2$ 2-Aminoacridine-7-carboxylic acid, 458.
$C_{14}H_{10}O_5N_2$ 6-Nitronaphthyl-1-maleamic acid, 391.
$C_{14}H_{10}O_6N_2$ 5-Nitrodiphenylamine-2:4′-dicarboxylic acid, 458.
$C_{14}H_{11}O_2N_3$ 3-Nitro-7-amino-5-methylacridine, 346.
$C_{14}H_{11}O_3Cl$ *m*-(*p*′-Chlorobenzyloxy)benzoic acid, 432.
$C_{14}H_{11}O_3Br$ *m*-(*p*′-Bromobenzyloxy)benzoic acid, 432.
$C_{14}O_{11}O_3F$ *m*-(*p*′-Fluorobenzyloxy)benzoic acid, 432.
$C_{14}H_{12}O_3N_2$ $a$-Nitroacetamidophenyl-$\beta$-(2-furyl)ethylenes, 451.
$C_{14}H_{13}ON$ Phenacylaniline, and its salts, 63.
$C_{14}H_{13}O_3N$ 2-Nitro-5-benzyloxytoluene, 49.
4-Nitro-*o*-tolyl benzyl ether, 432.
$C_{14}H_{12}N_2Cl$ *p*-Chloroacetophenone phenylhydrazone, 67.
$C_{14}H_{13}N_2Br$ Amino-10-methylacridinium bromides, 460.
$C_{14}H_{14}ON_2$ 5-Amino-5-hydroxy-10-methylacridane, 460.
$C_{14}H_{14}O_2N_2$ Acetamidomethoxyphenylpyridines, 410.
$C_{14}H_{14}O_3N_4$ 4′-Nitro-4-methoxy-3-methyl-3-methyldiazoaminobenzene, 223.
$C_{14}H_{14}O_4N_2$ Ethyl 2-keto-1-methyl-1:2-dihydroquinoxaline-3-pyruvate, 400.
Ethyl 3-methyl-4-quinazolonyl-2-pyruvate, 400.
$C_{14}H_{19}O_2N$ Dimethylbutylcarbinyl phenylurethane, 263.
2-Methylhex-3-en-5-yn-2-ol phenylurethane, 263.
$C_{14}H_{15}O_4N_3$ Ethyl 2-keto-1-methyl-1:2-dihydroquinoxaline-3-pyruvate oxime, 400.
$C_{14}H_{16}O_2N_2$ Phthalo-$\gamma$-($\gamma$-bromopropylamino)propylimide, hydrobromide of, 556.
$C_{14}H_{16}O_2N_2$ 2-Methyl-3-*n*-amylquinoxaline di-*N*-oxide, 325.
$C_{14}H_{19}ON_3$ 8-$\gamma$-Methylaminopropylamino-6-methoxyquinoline, and its salts, 562.
$C_{14}H_{21}ON$ $\gamma$-(*p*-*tert.*-Butylphenyl)butyramide, 145.

### 14 IV

$C_{14}H_{10}O_5N_2S$ 1:4-Diaminoanthraquinone-2-sulphonic acid, sodium salt, 47.
$C_{14}H_{11}ON_2Cl$ 2-Chloro-5-amino-7-methoxyacridine, 654.
$C_{14}H_{12}ONCl$ *p*-Chlorophenacylaniline, 63.
$C_{14}H_{12}O_4N_2Cl_4$ 2:3:5:6-Tetrachloro-1:4-diacetamidobenzene, 234.
$C_{14}H_{14}O_2N_2S$ Benzo-*m*-toluidide-6-sulphonamide, 79.
$C_{14}H_{17}N_2IS_2$ [2-(3-Methyldihydro-1:3-thiazine)][2-(3-methylbenzthiazole)]methincyanine iodide, 247.
$C_{14}H_{19}O_4N_2S$ 3-(*p*-Acetamidobenzenesulphonamido)homopiperidone, 40.
$C_{14}H_{20}O_2NCl$ 4-Chloro-2-nitro-3:5-dimethylphenyl *n*-hexyl ether, 445.
$C_{14}H_{21}O_4NS$ Mesitylenesulphonylalanine, ethyl ester, 378.

### 14 V

$C_{14}H_6O_6NBrS$ 4-Bromo-1-aminoanthraquinone-2-sulphonic acid, salts, 47.

## $C_{15}$ Group.

$C_{15}H_{11}N$ 5-Phenylquinoline, and its picrate, 444.
2-Pyridylnaphthalenes, and their picrates, 444.
$C_{15}H_{12}O_2$ 3′-Keto-4-acetoxy-1:2-*cyclo*pentenonaphthalene, 498.
$C_{15}H_{12}O_4$ *O*-Benzoyl-*r*-mandelic acid, 228.
2′:3′-Diketo-4′:6-dimethoxy-1:2-*cyclo*pentenonaphthalene, 501.
$a$-($\beta$-Styrylacryl)tetronic acid, 242.
$C_{15}H_{12}N_2$ Aminophenylquinolines, 317.
6-Pyridylquinaldines, 412.
$C_{15}H_{14}O_3$ *m*-$\beta$-Phenylethoxybenzoic acid, 432.
$C_{15}H_{14}O_6$ 2-Carboxy-4:6-dimethoxynaphthalene-1-acetic acid, 501.
$C_{15}H_{14}N_2$ Acetone diphenylenehydrazone, 660.
5-Dimethylaminoacridine, and its hydrochloride, 461.
1-3′-Quinolyl-2:5-dimethylpyrrole, 420.

$C_{15}H_{15}P$ 2-Phenyl-1:2:3:4-tetrahydro*iso*phosphinoline, 550.
$C_{15}H_{15}As$ 2-Phenyl-1:2:3:4-tetrahydro*iso*arsinoline, and its salts, 549.
$C_{15}H_{16}O_3$ 6-Piperonylidene-2-methyl*cyclo*hexanone, 662.
$C_{15}H_{16}O_4$ α-(δ-Phenylvaleryl)tetronic acid, 242.
$C_{15}H_{16}O_5$ Methyl 6-methoxy-5-methyl-1-tetralone-2-glyoxylate, 493.
$C_{15}H_{18}O_2$ 3′-Keto-6-hydroxy-2:5-dimethyl-1:2:3:4-tetrahydro-1:2-*cyclo*pentenonaphthalene-α, 496.
$C_{15}H_{18}O_3$ 6-Methoxy-2:5-dimethyl-3:4-dihydronaphthalene-1-acetic acid, 495.
$C_{15}H_{18}O_4$ Methyl 6-methoxy-2:5-dimethyl-1-tetralone-2-carboxylate, 494.
$C_{15}H_{18}O_6$ Tutin, 50.
$C_{15}H_{18}N_2$ Amino-4-*tert.*-butylpyridylbenzenes, 412.
$C_{15}H_{20}O$ 7:12-Dimethyl-1:2:3:4:12:13-hexahydroxanthen, 476.
$C_{15}H_{20}O_3$ 6-Methoxy-2:5-dimethyltetralin-1-acetic acid, 496.
α-2-Methoxy-4-methylbenzoyl-α-*n*-propylacetone, 434.
$C_{15}H_{20}O_6$ α- and β-Dihydrotutin, 143.
$C_{15}H_{22}O_3$ 3′:6-Diketo-2:5-dimethyldecahydro-1:2-*cyclo*pentenonaphthalene-x-α, 497.
Ethyl β-phenyl-ααβ-trimethyl-*n*-butyrate, 429.
$C_{15}H_{22}O_3$ *n*-Octyloxybenzoic acid, 432.
$C_{15}H_{24}O$ 3′:6-Dihydroxy-2:5-dimethyldecahydro*cyclo*pentenonaphthalene, 497.

## 15 III

$C_{15}H_{10}O_5N_2$ 4-Phthalo-3-nitro-*p*-anisidide, 411.
$C_{15}H_{10}NBr$ 4-Bromo-4′-cyanostilbene, 3.
$C_{15}H_{11}O_3N_3$ 5-Nitro-6-methoxy-8-α-pyridylquinoline, 411.
$C_{15}H_{13}ON_3$ 5-Acetamidoacridine, 457.
2-Keto-3-benzyl-1:2-dihydroquinoxaline, 397.
Methoxypyridylquinolines, and their picrates, 410.
$C_{15}H_{12}O_2N_2$ 3-Nitro-5:7-dimethylacridine, 347.
$C_{15}H_{12}O_3N_2$ 4-Phthalo-3-amino-*p*-anisidide, 411.
$C_{15}H_{12}O_5N_2$ 5:5′-Dinitro-2:2′-dihydroxy-3:3′-bishydroxymethylbenzophenone, 321.
$C_{15}H_{12}NCl$ 2-*p*-Chlorophenyl-5-methylindole, 64.
3-*p*-Chlorophenyl-1-methylindole, and its picrate, 66.
$C_{15}H_{12}ON_2$ 5-Amino-6-methoxy-8-α-pyridylquinoline, 412.
$C_{15}H_{13}O_2N$ Benzoylphenacylamine, 317.
$C_{15}H_{13}O_3Cl$ Furfurylidene-6-chloro-4-methoxy-3-methylacetophenone, 500.
$C_{15}H_{14}O_3N_2$ 4-Pyridylacetoacetanilide, 413.
$C_{15}H_{14}O_2N_2$ 4-Nitro-2-acetyl-4′-methyldiphenylamine, 347.
$C_{15}H_{15}OCl$ 4-Chloro-3:5-dimethylphenyl benzyl ether, 445.
$C_{15}H_{15}O_3N$ 4-Nitro-*o*-tolyl *p*-methylbenzyl ether, 432.
$C_{15}H_{15}O_4Cl$ 2-(4′-Chloro-6′-methoxy-*m*-tolyl)furan-5-β-propionic acid, 500.
$C_{15}H_{15}O_5Br$ Bromohydropicrotoxinin, 51, 143.
$C_{15}H_{15}N_2Cl$ 3-Amino-5-methylacridine methochloride, 346.
$C_{15}H_{15}Cl_2As$ 2-Phenyl-1:2:3:4-tetrahydro*iso*arsinoline dichloride, 549.
$C_{15}H_{15}SAs$ 2-Phenyl-1:2:3:4-tetrahydro*iso*arsinoline sulphide, 549.
$C_{15}H_{16}O_2N_2$ Nitro-4-*tert.*-butylpyridylbenzenes, and their picrates, 412.
$C_{15}H_{16}N_3Cl$ 3:7-Diamino-5-methylacridine methochloride, 346.
$C_{15}H_{17}O_2N_5$ 4-Methoxy-3-methylhydrazobenzene-*N*-diazocarbonamide, 223.
$C_{15}H_{17}O_5Br$ Bromohydrotutin, 51, 143.
$C_{15}H_{21}ON_3$ 8-γ-Ethylaminopropylamino-6-methoxyquinoline, and its salts, 562.
1-Keto-7-*tert.*-butyl-1:2-3:4-tetrahydronaphthalene semicarbazone, 145.
$C_{15}H_{21}O_2N_3$ 8-β-Hydroxyethyl-γ-aminopropylamino-6-methoxyquinoline, and its salts, 564.
$C_{15}H_{21}O_3N_3$ β-(*p-tert.*-Butylbenzoyl)propionic acid semicarbazone, 145.
$C_{15}H_{22}ON_4$ 8-β′-Aminoethyl-γ-aminopropylamino-6-methoxyquinoline, and its salts, 563.

## 15 IV

$C_{15}H_{11}ON_2Cl$ Nitroso-2-*p*-chlorophenyl-5-methylindole, 64.
$C_{15}H_{11}O_4NBr_2$ 2:6-Dibromo-4-ethylphenyl *p*-nitrobenzoate, 527.
$C_{15}H_{12}O_4NBr$ Bromo-4-ethylphenyl *p*-nitrobenzoates, 526.
$C_{15}H_{13}O_2N_2S$ 1-Amino-4-methylaminoanthraquinone-2-sulphonic acid, sodium salt, 47.
$C_{15}H_{14}ONCl$ *p*-Chlorophenacyl-*N*-methylaniline, 65.
*p*-Chlorophenacyl-*p*-toluidine, 63.
$C_{15}H_{14}O_2NCl$ 4-Chloro-2-nitro-3:5-dimethylphenyl benzyl ether, 445.
$C_{15}H_{14}O_6N_2S$ 4-Nitrobenzenesulphonylbenzimino-ether, 103.
$C_{15}H_{15}O_3N_2S$ 4-Acetamidobenzenesulphonylbenzamidine, 103.
$C_{15}H_{16}O_3N_2S$ Aceto-*m*-toluidide-6-sulphonanilide, 78.
4-Aminobenzenesulphonylbenzimino-ether, 103.
$C_{15}H_{16}O_7NNa$ Sodioethyl *p*-nitrophenylacetylmalonate, 69.
$C_{15}H_{19}N_2IS_2$ [2-(3-Methyldihydro-1:3-thiazine)][2-(3-ethylbenzthiazole)]methincyanine iodide, 248.
$C_{15}H_{20}O_5N_4S_2$ αα′-Di-(*p*-aminobenzenesulphonamido)*iso*propyl alcohol, 608.
$C_{15}H_{21}O_4NS$ *N*-Mesitylenesulphonyl-*N*-β-methylallylglycine, 377.
$C_{15}H_{25}N_2IS_2$ Bis-2-(3-ethyldihydro-1:3-thiazine)trimethincyanine iodide, 249.

## 15 V

$C_{15}H_{13}O_3NClBr$ 4-Chloro-2-nitro-3:5-dimethylphenyl *p*-bromobenzyl ether, 445.
$C_{15}H_{16}O_2NClS$ *p*-Toluenesulphonylchloro-*N*-ethylaniline, 65.
$C_{15}H_{18}N_2ClIS_2$ [2-(3-Methyldihydro-1:3-thiazine)][2-(6-chloro-3-ethylbenzthiazole)]methincyanine iodide, 248

$C_{15}H_{19}ON_2IS$ 2-β-Acetanilidovinyldihydro-1:3-thiazine methiodide, 247.
$C_{15}H_{15}N_2ISSe$ [2-(3-Methyldihydro-1:3-thiazine)][2-(3-ethylbenzselenazole)]methincyanine iodide, 248.
$C_{15}H_{22}O_4NClS$ Ethyl *N*-*p*-toluenesulphonyl-*N*-β-chloro*iso*butylaminoacetate, 377.

## $C_{16}$ Group.

$C_{16}H_{18}$ βγ-Diphenyl-*n*-butane, 100.
$C_{16}H_{34}$ 2:6:11-Trimethyl-*n*-tridecane, 267.

### 16 II

$C_{16}H_8N_2$ 4:4′-Dicyanotolane, 3.
$C_{16}H_{10}N_2$ Dicyanostilbenes, 3.
$C_{16}H_{13}N$ 2:4-Diphenylpyrrole, 594.
$C_{16}H_{13}N_3$ 2-Cyano-4-amidinostilbene, 3.
$C_{16}H_{14}O_3$ *p*-Benzoyloxypropiophenone, 612.
4-Methoxy-1:2-*cyclo*pentadienonaphthalene-3′-acetic acid, 499.
$C_{16}H_{14}O_4$ 3′-Keto-4-acetoxy-5-methoxy-1:2-*cyclo*pentenonaphthalene, 499.
$C_{16}H_{14}N_2$ 5-Amino-2:4-diphenylpyrrole, 595.
2′:6′-Dimethylpyridylquinolines, 415.
Lutidylquinolines, and their picrates, 415.
$C_{16}H_{14}N_4$ 4:4′-Diamidinotolane, hydrochloride of, 3.
$C_{16}H_{14}Br_2$ 4:4′-Dibromo-αβ-dimethylstilbenes, 100.
$C_{16}H_{14}Br_4$ 4:4′-β:γ-Tetrabromo-βγ-diphenyl-*n*-butane, 100.
$C_{16}H_{15}N$ 2-Phenyl-5:7-dimethylindole, and its picrate, 64.
2-Phenyl-1-ethylindole, 67.
3-Phenyl-1-ethylindole, 66.
$C_{16}H_{15}Br_3$ 4:4′:β-Tribromo-βγ-diphenyl-*n*-butane, 101.
$C_{16}H_{16}O_3$ 4-Methoxy-1:2-*cyclo*pentenonaphthalene-3′-acetic acid, 499.
*m*-*p*-Phenyl-*n*-propoxybenzoic acid, 432.
$C_{16}H_{16}O_4$ 1-Carboxymethylene-6-methoxy-2:5-dimethyltetralin-2-carboxylic anhydride, 494.
$C_{16}H_{16}N_4$ *cis*-4:4′-Diamidinostilbene, 4.
$C_{16}H_{16}Br_2$ 4:4′-Dibromo-βγ-diphenyl-*n*-butanes, 100.
$C_{16}H_{16}O_3$ 4-Methoxy-7:8-dihydro-1:2-*cyclo*pentenonaphthalene-3′-acetic acid, 500.
6-Piperonylidene-2:2-dimethyl*cyclo*hexanone, 662.
$C_{16}H_{18}O_4$ 2-Carboxy-6-methoxy-2:5-dimethyltetralin-1-acetic anhydrides, 495.
$C_{16}H_{20}O_5$ 2-Carboxy-6-methoxy-2:5-dimethyltetralin-1-acetic acids, 494.
Methyl α-2-carboxy-6-hydroxy-2:5-dimethyltetralin-1-acetate, 496.
$C_{16}H_{22}O_3$ α-2-Methoxy-4-methylbenzoyl-α-*n*-butylacetone, 435.
$C_{16}H_{24}O_3$ *n*-Nonyloxybenzoic acid, 432.

### 16 III

$C_{16}H_7N_2Br$ α-Bromo-4:4′-dicyanostilbene, 3.
$C_{16}H_{10}N_2Br_2$ αβ-Dibromo-4:4′-dicyano-αβ-diphenylethane, 3.
$C_{16}H_{11}O_2N_3$ 4-Nitro-1:3-dipyridylbenzenes, 406.
$C_{16}H_{11}O_4N_3$ 1-Nitro-6:17-diketo-6:8:15:17-tetrahydro-7:16-diazanaphthacene, 659.
$C_{16}H_{12}ON_2$ 5-Nitroso-2:4-diphenylpyrrole, and its salts, 594.
$C_{16}H_{12}O_2N_2$ 6:17-Diketo-6:8:15:17-tetrahydro-7:16-diazanaphthacene, 658.
$C_{16}H_{12}O_7N_2$ *p*-Nitrophenylacetic anhydride, 69.
$C_{16}H_{13}O_2N_3$ 1-Amino-6:17-diketo-6:8:15:17-tetrahydro-7:16-diazanaphthacene, 659.
$C_{16}H_{13}O_3N$ 5-Benzyloxyindole-2-carboxylic acid, 49.
$C_{16}H_{13}O_3N_3$ 3-Nitro-7-acetamido-5-methylacridine, 346.
$C_{16}H_{14}ON_2$ 3-Acetamido-5-methylacridine, 346.
3-Nitroso-2-phenyl-1-ethylindole, 67.
$C_{16}H_{14}O_2N_2$ Methyl pyruvate diphenylenehydrazone, 660.
$C_{16}H_{14}O_3N_2$ 2-*o*-Carboxybenzoyl-1:2:3:4-tetrahydrophthalazine, and its sodium salt, 658.
$C_{16}H_{14}O_5N_2$ γ-Nitro-β-(*m*-nitrophenyl)butyrophenone, 592.
$C_{16}H_{14}NCl$ 2-*p*-Chlorophenyl-1-ethylindole, 67.
3-*p*-Chlorophenyl-1-ethylindole, 66.
$C_{16}H_{15}O_4N$ γ-Nitro-β-(*m*-hydroxyphenyl)butyrophenone, 593.
$C_{16}H_{15}O_4N_3$ Nitroacetamido-2-acetyldiphenylamines, 346.
$C_{16}H_{16}ON_2$ 1-6′-Methoxy-8′-quinolyl-2:5-dimethylpyrrole, 420.
$C_{16}H_{16}O_3N_2$ γ-Nitro-β-phenylbutyrophenone oxime, 595.
$C_{16}H_{17}ON$ Phenacyl-*N*-ethylaniline, 65.
Phenyl-2-aminophenylallylcarbinol, 451.
$C_{16}H_{17}O_4Cl$ Methyl 2-(4′-chloro-6′-methoxy-*m*-tolyl)furan-5-β-propionate, 500.
$C_{16}H_{17}N_2Cl$ 3-Amino-5:7-dimethylacridine methochloride, 347.
$C_{16}H_{18}IP$ 2-Phenyl-1:2:3:4-tetrahydro*iso*phosphinoline methiodide, 550.
$C_{16}H_{18}IAs$ 2-Phenyl-1:2:3:4-tetrahydro*iso*arsinoline methiodide, 549.
$C_{16}H_{19}O_2N$ 4:4′-Diethoxydiphenylamine, 65.
$C_{16}H_{23}ON_3$ 8-γ-Propylaminopropylamino-6-methoxyquinolines, and their salts, 562.
$C_{16}H_{24}ON_4$ 8-Bis-γ-aminopropylamino-6-methoxyquinoline, trihydrochloride of, 556.
$C_{16}H_{23}O_2N_3$ 8-β-Hydroxyethylmethyl-γ-aminopropylamino-6-methoxyquinoline, and its salts, 565.
$C_{16}H_{23}O_4N$ Ethyl 2-β-carbethoxyethyl-$\Delta^1$-*cyclo*hexene-1-cyanoacetate, 502.
$C_{16}H_{24}ON_4$ 8-γ-Aminopropyl-γ-aminopropylamino-6-methoxyquinoline, trihydrochloride of, 556.
8-γ′-Aminopropyl-γ-aminopropylamino-6-methoxyquinoline, and its salts, 564.
R. 63, and its salts, 558.

### 16 IV

$C_{16}H_7O_3N_2Cl_4$ 2:3:5:6-Tetrachloro-4-nitrobenzeneazo-β-naphthol, 234.
$C_{16}H_8ON_2Cl_4$ 2:3:5:6-Tetrachlorobenzeneazo-β-naphthol, 234.
$C_{16}H_8O_2N_2Cl_4$ 2:3:5:6-Tetrachloro-4-hydroxybenzeneazo-β-naphthol, 235.

$C_{16}H_9ON_2Cl_4$ 2:3:5:6-Tetrachloro-4-aminobenzeneazo-β-naphthol, 234.
$C_{16}H_9O_2N_2Cl_3$ 2:3:5-Trichloro-6-hydroxybenzeneazo-β-naphthol, 237.
$C_{16}H_{11}ON_2Cl$ 4-Chloro-1-benzeneazo-2-naphthol, 469.
$C_{16}H_{11}ON_2Br$ 4-Bromo-1-benzeneazo-2-naphthol, 469.
$C_{16}H_{11}ON_2I$ 4-Iodo-1-benzeneazo-2-naphthol, 469.
$C_{16}H_{11}ON_2Cl$ 3-Nitroso-2-*p*-chlorophenyl-1-ethylindole, 68.
$C_{16}H_{14}ON_2Cl$ 1-Phenyl-3-methylquinoxaline-2-aldoxime chloride, 400.
$C_{16}H_{14}O_2NCl$ Acetyl-*p*-chlorophenacylaniline, 63.
$C_{16}H_{15}ONCl_2$ *p*-Chloro-(*p*′-chlorophenacyl)-*N*-ethylaniline, 65.
$C_{16}H_{16}ONCl$ *p*-Chlorophenacyl-2:4-dimethylaniline, 63.
*p*-Chlorophenacyl-*N*-ethylaniline, and its salts, 65.
$C_{16}H_{19}O_2NS$ *p*-Toluenesulphonyl-*N*-ethyl-*p*-toluidine, 65.
$C_{16}H_{19}N_2IS$ [2-(3-Methyldihydro-1:3-thiazine)][2-(1-methylquinoline)]methincyanine iodide, 248.
[2-(3-Methyldihydro-1:3-thiazine)][4-(1-methylquinoline)]methincyanine iodide, 248.
$C_{16}H_{21}N_2IS_2$ [2-(3-Ethyldihydro-1:3-thiazine)][2-(3-ethylbenzthiazole)]methincyanine iodide, 247.
$C_{16}H_{22}ON_2Cl$ 5-Chloro-8-β-diethylaminoethylamino-6-methoxyquinoline, 556.

### 16 V

$C_{16}H_{20}N_2ClIS_2$ [2-(3-Ethyldihydro-1:3-thiazine)][2-(5-chloro-3-ethylbenzthiazole)]methincyanine iodide, 248.
$C_{16}H_{21}ON_2IS$ [2-(3-Ethyldihydro-1:3-thiazine)][2-3-ethylbenzoxazole)]methincyanine iodide, 247.
$C_{16}H_{21}N_2ISSe$ [2-(3-Ethyldihydro-1:3-thiazine)][2-(3-ethylbenzselenazole)]methincyanine iodide, 248.

## $C_{17}$ Group.

$C_{17}H_{13}N_4$ 4-Amino-5-cyano-2:6-diphenylpyrimidine, 390.
$C_{17}H_{14}O$ Dibenzylideneacetone, compounds of, with *s*-trinitrobenzene, 463.
$C_{17}H_{14}N_2$ 4-Pyridyldiphenylamine, and its picrate, 418.
$C_{17}H_{17}N$ 2-Phenyl-5-methyl-1-ethylindole, 67.
3-Phenyl-5-methyl-1-ethylindole, and its picrate, 66.
$C_{17}H_{18}N_2$ 5-Butylaminoacridine, and its hydrochloride, 654.
$C_{17}H_{20}O_3$ 6-Piperonylidene-2-methyl-2-ethyl*cyclo*hexanone, 662.
$C_{17}H_{20}O_7$ Acetyltutin, 51.
$C_{17}H_{22}O_4$ 4:6-Dimethoxy-5:6:7:8-tetrahydro-1:2-*cyclo*pentenonaphthalene-3′-acetic acid, 499.
$C_{17}H_{22}O_5$ α-2-Carbomethoxy-6-hydroxy-2:5-dimethyltetralin-1-acetic acid, 496.
$C_{17}H_{24}O$ 2:2-Dimethyl-3-(γ-methyl-$\Delta^{\gamma}$-pentenyl)chroman, 476.
$C_{17}H_{24}O_3$ α-2-Methoxy-4-methylbenzoyl-α-*n*-amylacetone, 435.
$C_{17}H_{28}O_4$ Methyl-2-carbomethoxy-6-hydroxy-2:5-dimethyldecalin-2-acetate, 496.
$C_{17}H_{34}O_2$ Methyldi-*n*-heptylacetic acid, 618.

### 17 III

$C_{17}H_{12}O_4N_2$ 2-Keto-1-phenyldihydroquinoxaline-3-pyruvic acid, 400.
$C_{17}H_{13}ON$ 2:4-Diphenylpyrrole-5-aldehyde, 597.
$C_{17}H_{13}O_2Br$ 3-Bromo-4-keto-1-phenyl-1:2:3:4-tetrahydro-2-naphthoic acid, 13.
$C_{17}H_{14}ON_2$ Acetamidophenylquinolines, 317.
2:4-Diphenylpyrrole-5-aldoxime, 597.
$C_{17}H_{14}O_2N_2$ 5-Nitroso-2-phenyl-4-anisylpyrrole, and its salts, 595.
6-Nitro-4-*p*-toluneazo-1-naphthylamine, 393.
$C_{17}H_{15}ON$ 2:4-Diphenylpyrrole-5-carbinol, 597.
Phenylanisylpyrroles, 594.
$C_{17}H_{15}O_2N$ Hex-3-en-5-yn-2-ol β-naphthylurethane, 263.
$C_{17}H_{15}O_3N$ Methyl 5-benzyloxyindole-2-carboxylate, 49.
$C_{17}H_{16}ON_2$ 3-Acetamido-5:7-dimethylacridine, 347.
3-Nitroso-2-phenyl-5-methyl-1-ethylindole, 67.
$C_{17}H_{16}O_{11}N_2$ *d*(−)-Arabinose 2:4-dinitrophenylosazone, 628.
$C_{17}H_{16}NCl$ 2-*p*-Chlorophenyl-5-methyl-1-ethylindole, 68.
3-*p*-Chlorophenyl-5-methyl-1-ethylindole, and its picrate, 66.
2-*p*-Chlorophenyl-1-*n*-propylindole, 68.
$C_{17}H_{17}ON$ Phenylanisylpyrrolines, and their picrates, 594.
$C_{17}H_{17}O_4N$ γ-Nitro-β-*p*-anisylbutyrophenone, 593.
γ-Nitro-β-phenyl-*p*-methoxybutyrophenone, 593.
$C_{17}H_{18}O_6N_2$ 7-Methylnon-7-en-5-yn-4-ol 3:5-dinitrobenzoate, 267.
$C_{17}H_{19}ON$ β-(*N*-Methylanilino)anethole, 611.
Phenyl-*N*-ethyl-*p*-toluidine, 65.
$C_{17}H_{19}O_3N_3$ β-Hydroxypropylphenylcarbamide phenylurethane, 377.
$C_{17}H_{20}O_5N_4$ 2:4-Dinitro-*N*-γ-phenoxypropyl-β-aminoethylaniline, hydrochloride of, 556.
$C_{17}H_{22}O_4N_4$ *cis*-2-Keto-9-methyldecalin 2:4-dinitrophenylhydrazone, 502.
$C_{17}H_{24}O_6N_2$ 7-Methylnonanol 3:5-dinitrobenzoates, 267.
Methyloctylcarbinyl 3:5-dinitrobenzoate, 265.
Propylhexylcarbinyl 3:5-dinitrobenzoate, 265.
$C_{17}H_{25}ON_3$ 8-γ-Butylaminopropylamino-6-methoxyquinolines, and their salts, 563.
8-γ-Diethylaminopropylamino-6-methoxyquinoline, and its salts, 564.
8-γ-Methylpropylaminopropylamino-6-methoxyquinoline, and its salts, 564.
$C_{17}H_{26}ON_4$ 8-δ′-Amino-*n*-butyl-γ-aminopropylamino-6-methoxyquinoline, and its salts, 564.
$C_{17}H_{27}ON_3$ 7-Methylnonanone phenylsemicarbazones, 267.
$C_{17}H_{35}ON$ Methyldi-*n*-heptylacetamide, 618.

### 17 IV

$C_{17}H_8O_4N_2Cl_4$ 2:3:5:6-Tetrachloro-4-nitro-2′-hydroxy-3′-naphthanilide, 234.
$C_{17}H_9O_2NCl_4$ 2:3:5:6-Tetrachloro-2′-hydroxy-3′-naphthanilide, 234.

$C_{17}H_{10}O_2N_2Cl_4$ 2:3:4:5-Tetrachloro-6-methoxybenzeneazo-β-naphthol, 237.
2:3:5:6-Tetrachloro-4-methoxybenzeneazo-β-naphthol, 234.
6-*p*-Toleneazo-2:4-bisdichloromethylene-1:3-benzdioxin, 321.
$C_{17}H_{11}O_2N_2Cl_3$ 2:3:5-Trichloro-6-methoxybenzeneazo-β-naphthol, 236.
$C_{17}H_{13}O_6N_4S$ 2:4:6-Trinitro-*p*-toluenesulphon-1-naphthalide, 393.
$C_{17}H_{14}O_4N_2S$ 6-Nitro-*p*-toluenesulphon-1-naphthalide, 391.
$C_{17}H_{15}ON_2Cl$ 3-Nitroso-2-*p*-chlorophenyl-1-*n*-propylindole, 68.
$C_{17}H_{15}O_2N_3S$ *p*-Toluenesulphonylquinoline carboxyhydrazides, 415.
$C_{17}H_{17}O_3N_3S$ *N*-Benzenesulphonyl-*N*-acetonylglycine 2:4-dinitrophenylhydrazone, 377.
$C_{17}H_{18}ONCl$ *p*-Chlorophenacyl-*N*-ethyl-*p*-toluidine, and its salts, 65.
$C_{17}H_{18}O_4N_2S$ 4-Acetamidobenzenesulphonylbenzimino-ether, 103.
$C_{17}H_{18}O_3N_2As$ 2-Methyl-1:2:3:4-tetrahydro*iso*arsinoline methosulphate, 549.
$C_{17}H_{21}O_3Cl_2P$ 6″-*O*-Dichlorophosphoryl-2:2:5′:4″-tetramethyl-3′:4′:5′:6′-tetrahydrodibenzopyran, 286.
$C_{17}H_{21}N_2IS$ [2-(3-Methyldihydro-1:3-thiazine)][2-(1-ethylquinoline)]methincyanine iodide, 248.
[2-(3-Methyldihydro-1:3-thiazine)][4-(1-ethylquinoline)]methincyanine iodide, 248.
[2-(3-Methyldihydro-1:3-thiazine)][2-(3-ethylbenzthiazole)]trimethincyanine iodide, 249.

### 17 V

$C_{17}H_{10}O_2N_2Cl_3Br$ 2:3:5-Trichloro-4-bromo-6-methoxybenzeneazo-β-naphthol, 237.
$C_{17}H_{12}O_4N_2BrS$ 1-Bromo-6-nitro-*p*-toluenesulphon-2-naphthalide, 392.
$C_{17}H_{21}ON_2IS$ [2-(3-Methyldihydro-1:3-thiazine)][2-(3-ethylbenzoxazole)]trimethincyanine iodide, 249.
$C_{17}H_{22}ON_3IS_2$ [2-(3-Methyldihydro-1:3-thiazine)][2-(6-acetamido-3-ethylbenzthiazole)]methincyanine iodide, 248.

## $C_{18}$ Group.

$C_{18}H_{12}N_2$ Pyridylacridines, 417.
$C_{18}H_{14}N_2$ Amino-9-phenylcarbazoles, 661.
4:4′-Dicyano-αβ-dimethylstilbene, 101.
$C_{18}H_{15}N$ 1:9-(2′:3′:4′:5′-Tetrahydrophenylene)carbazole, and its picrate, 660.
$C_{18}H_{16}O_2$ 3-Benzyl-2:7-dimethylchromone, 435.
Benzylidene-*p*-anisylideneacetone, compounds of, with *s*-trinitrobenzene, 463.
$C_{18}H_{16}N_2$ 4:4′-Dicyano-βγ-diphenyl-*n*-butanes, 101.
$C_{18}H_{18}O_2$ Dienœstrol, 609.
$C_{18}H_{18}O_5$ Phenylphenacyl *dl-erythro*-αβ-dihydroxybutyrate, 467.
$C_{18}H_{18}N_2$ 8-Pyridyl-5-*tert.*-butylquinoline, 412.
$C_{18}H_{20}O_3$ γγ-Bis-4-hydroxyphenylhexan-3-one, 612.
$C_{18}H_{20}N_4$ *trans*-4:4′-Diamidino-αβ-dimethylstilbene, and its dihydrochloride, 101.
$C_{18}H_{22}O$ *cis*-Benzylidene-2-keto-9-methyldecalin, 502.
$C_{18}H_{22}O_4$ γδ-Bis-4-hydroxyphenylhexane-γδ-diol, 612.
Methyl 3′-keto-6-methoxy-2:5-dimethyl-1:2:3:4-tetrahydro-1:2-*cyclo*pentenonaphthalene-2′-carboxylate 496.
$C_{18}H_{23}O_5$ Methyl 1-carbomethoxymethylene-6-methoxy-2:5-dimethyltetralin-2-carboxylate, 494.
$C_{18}H_{23}N_4$ 4:4′-Diamidino-βγ-diphenylbutane, and its dihydrochloride, 101.
$C_{18}H_{24}O_5$ Methyl 2-carbomethoxy-6-methoxy-2:5-dimethyltetralin-1-acetates, 494.
$C_{18}H_{24}O_6$ Methyl 1-hydroxy-6-methoxy-2-carbomethoxy-2:5-dimethyltetralin-1-acetate, 494.
$C_{18}H_{34}O_2$ Elaidic acid, oxidation of, by hydrogen peroxide in acetic acid, 37.
Oleic acid, oxidation of, by hydrogen peroxide in acetic acid, 37.

### 18 III

$C_{18}H_{10}O_6N_2$ 1:3-Dihydroxy-2-2′:4′-dinitrophenylnaphthalene, 69.
$C_{18}H_{12}ON_2$ Pyridylacridones, 418.
$C_{18}H_{13}O_2N_3$ Nitro-9-phenylcarbazoles, 661.
$C_{18}H_{14}ON_2$ *o*-Benzamidophenylpyridines, and its picrates, 317.
$C_{18}H_{14}O_2N_2$ Pyridyldiphenylamine-2′-carboxylic acids, 418.
$C_{18}H_{14}O_3N_4$ 3-(2-Keto-1-methyldihydroquinoxalinyl)-3-(2-ketodihydroquinoxalinyl)methane, 400.
2-(3-Methyl-4-quinazolonyl)-3-(2-ketodihydroquinoxalyl)methane, 400.
$C_{18}H_{14}O_6N_2$ 3-Hydroxy-1-ethoxy-2-2′:4′-dinitrophenylnaphthalene, 69.
$C_{18}H_{15}O_2N$ 2-Phenyl-4-*p*-anisylpyrrole-5-aldehyde, 597.
$C_{18}H_{16}ON_2$ 5-Acetamido-2:4-diphenylpyrrole, 595.
$C_{18}H_{16}O_2N_2$ 4-Methoxy-2-methylbenzeneazo-β-naphthol, 223.
2-Phenyl-4-*p*-anisylpyrrole-5-aldoxime, 597.
$C_{18}H_{16}O_7N_2$ Ethyl α-2:4-dinitrophenyl-γ-phenylacetoacetate, 69.
$C_{18}H_{17}O_3N$ 3-Methylhex-3-en-5-yn-2-ol α-naphthylurethane, 263.
$C_{18}H_{17}O_2N_3$ 3:7-Diacetamido-5-methylacridine, 346.
$C_{18}H_{18}O_2N_2$ Ethyl acetoacetate diphenylenehydrazone, 660.
$C_{18}H_{18}O_5N_4$ 6-Methoxy-5-methyl-1-tetralone 2:4-dinitrophenylhydrazone, 493.
$C_{18}H_{18}O_6N_4$ β-Benzoyl-αα-dimethylpropionic acid 2:4-dinitrophenylhydrazone, 428.
$C_{18}H_{18}NCl$ 2-*p*-Chlorophenyl-1-*iso*butylindole, 68.
3-*p*-Chlorophenyl-1-*iso*butylindole, 66.
$C_{18}H_{19}ON$ Phenyl-2-acetamidophenylallylcarbinol, 451.
$C_{18}H_{19}O_2N_3$ β-Benzoyl-α-(*p*-acetamidophenyl)propionitrile, 593.
$C_{18}H_{19}O_3N$ γ-Nitro-β-phenylhexophenone, 595.
$C_{18}H_{20}O_3N_2$ γ-Nitro-β-(*p*-dimethylaminophenyl)butyrophenone, 593.
$C_{18}H_{21}O_2N_3$ 8-γ-Furfurylaminopropylamino-6-methoxyquinoline, and its salts, 563.
$C_{18}H_{21}O_3N_3$ γ-Nitro-β-(*p*-dimethylaminophenyl)butyrophenone oxime, 593.
$C_{18}H_{23}ON_4$ 8-ε-Amino-*n*-amyl-γ-aminopropylamino-6-methoxyquinoline, and its salts, 564.

### 18 IV

$C_{18}H_{11}O_2NCl_4$ 2:3:5:6-Tetrachloro-4-methoxy-2′-hydroxy-3′-naphthanilide, 235.
$C_{18}H_{12}O_6N_2S_2$ Di-4-nitrobenzenesulphonanilide, 103.
$C_{18}H_{14}O_2N_4Cl$ 3-(2-Keto-1-methyldihydroquinoxalyl)-3-(2-ketodihydroquinoxalyl)methane hydrochloride, 401.
$C_{18}H_{17}ON_2Cl$ 3-Nitroso-2-*p*-chlorophenyl-1-*iso*butylindole, 68.
$C_{18}H_{18}ONCl$ *p*-Chlorophenacyl-*N*-*iso*butylaniline, 65.
$C_{18}H_{19}N_2IS_2$ [2-(3-Methyldihydro-1:3-thiazine)][2-(3-methyl-4:5-benzbenzthiazole)]methincyanine iodide, 247.
$C_{18}H_{23}N_2IS$ [2-(3-Ethyldihydro-1:3-thiazine)][2-(1-ethylquinoline)]methincyanine iodide, 248.
[2-(3-Ethyldihydro-1:3-thiazine)][4-(1-ethylquinoline)]methincyanine iodide, 248.
$C_{18}H_{24}O_2NBr$ Phthalobromodecylimide, 558.
$C_{18}H_{24}O_8N_4S$ 6-Acetamido-4-triacetyl-*d*-xylosidamino-2-methylthiopyrimidine, 573.

## $C_{19}$ Group.

$C_{19}H_{13}N_3$ *p*-Dipyridylbenzene, 406.
6:8-Dipyridylquinolines, 406.
6-α-Pyridyl-8-α(β and γ)-pyridylquinoline, 405.
$C_{19}H_{14}N_2$ Anilinoacridines, 461.
$C_{19}H_{16}O_3$ 4′-Methoxy-2-styryl-7-methylchroman, 434.
$C_{19}H_{18}O_8$ Dianisylideneacetone, compounds of, with *s*-trinitrobenzene, 463.
$C_{19}H_{16}O_4$ α-Benzoyl-α-2-methoxy-4-methylbenzoylacetone, 435.
$C_{19}H_{20}O_2$ Dienœstrol methyl ether, 612.
$C_{19}H_{20}O_3$ α-2-Methoxy-4-methylbenzoyl-α-benzylacetone, 435.
$C_{19}H_{29}N_3$ 5-*cyclo*Hexylaminoacridine, and its hydrochloride, 654.
$C_{19}H_{26}O_5$ Methyl α-2-carbomethoxy-6-methoxy-2:5-dimethyltetralin-1-β-propionate, 496.
$C_{19}H_{28}O_3$ 4-Acetoxy-$\Delta^5$-androsten-3(β)-ol-17-one, 138.
*cis*-$\Delta^5$-Androstene-3:4-diol-17-one, 138.
$C_{19}H_{30}O_3$ *n*-Dodecyloxybenzoic acid, 432.
$C_{19}H_{34}O_4$ Methyl hydroperoxido-oleate, 120.

### 19 III

$C_{19}H_{16}O_2N_4$ Bis-3-(2-keto-1-methyl-1:2-dihydroquinoxalinyl)methane, 400.
2-(3-Methyl-4-quinazolonyl)-3-(2-keto-1-methyldihydroquinoxalyl)methane, 400.
$C_{19}H_{16}O_3N_4$ Acetyl-6-nitro-4-*p*-tolueneazo-1-naphthylamine, 393.
$C_{19}H_{16}O_4N_2$ Ethyl 2-keto-1-phenyl-1:2-dihydroquinoxaline-3-pyruvate, 400.
$C_{19}H_{19}ON_3$ [2-(3-Keto-1:4-dimethyldihydroquinoxaline)][(4-dimethylaminophenyl)]dimethylcyanine, 396.
$C_{19}H_{20}O_5N_4$ 6-Methoxy-2:5-dimethyl-1-tetralone 2:4-dinitrophenylhydrazone, 494.
$C_{19}H_{20}O_6N_2$ Ethyl 4-*p*-nitrophenyl-2:6-dimethylpyridine-3:5-dicarboxylate, 416.
$C_{19}H_{20}O_6N_4$ Methyl β-benzoyl-αα-dimethylpropionate 2:4-dinitrophenylhydrazone, 428.
$C_{19}H_{22}O_4N_2$ Ethyl 4-*p*-aminophenyl-2:6-dimethylpyridine-3:5-dicarboxylate, 416.
$C_{19}H_{25}O_3N$ Delatine, and its hydrochloride, 140.
$C_{19}H_{27}ON_3$ 8-γ-*cyclo*Hexylaminopropylamino-6-methoxyquinoline, and its hydrogen oxalate, 563.

### 19 IV

$C_{19}H_{14}O_3N_2Cl_3$ 2:3:6-Trichloro-5-methoxy-4-acetamidobenzeneazo-β-naphthol, 237.
$C_{19}H_{14}O_5N_2S$ *N*-*p*-Nitrobenzenesulphonyl-*o*-phenylbenzimino-ether, 103.
$C_{19}H_{20}ON_2I$ [2-(3-Hydroxy-1-methylquinoxaline)][(4-dimethylaminophenyl)]dimethincyanine iodide, 396.
$C_{19}H_{24}O_7N_4S_2$ αα′-Di-(*p*-acetamidobenzenesulphonamido)*iso*propyl alcohol, 608.

### 19 V

$C_{19}H_{19}ON_2IS$ [2-(1-Methylbenzthiazole)][2-(3-keto-1:4-dimethyl-3:4-dihydroquinoxaline)]methincyanine iodide, 399.
$C_{19}H_{21}ON_2IS$ [2-(3-Methyldihydro-1:3-thiazine)][2-(3-6:7-benzbenzoxazole)]methincyanine iodide, 247.

## $C_{20}$ Group.

$C_{20}H_{12}$ Benzpyrene, determination of, 312.

### 20 II

$C_{20}H_{14}N_2$ Benzylideneaminoacridines, 460.
3:4-Diphenylcinnoline, 450.
$C_{20}H_{17}N$ α-(2-Aminophenyl)-αβ-diphenylethylenes, 450.
$C_{20}H_{18}O_3$ 4′-Methoxy-2-styryl-3:7-dimethylchromone, 434.
$C_{20}H_{22}O_2$ Dienœstrol dimethyl ether, 612.
$C_{20}H_{24}N_2$ 5-Heptylaminoacridine, hydrochloride of, 654.
$C_{20}H_{26}O_2$ αδ-Di-*p*-anisyl-βγ-dimethylbutane, 611.
$C_{20}H_{27}N_3$ 8-ω-Cyanodecylaminoquinoline, 560.
$C_{20}H_{28}O_3$ 6′′-Hydroxy-4′′-*n*-butoxy-2:2:5′-trimethyl-3′:4′:5′:6′-tetrahydrodibenzopyran, 286.
$C_{20}H_{30}N_4$ 8-ω-Guanyldecylaminoquinoline, and its hydrochloride, 560.
$C_{20}H_{34}O_2$ Ethyl linolenate, 546.

### 20 III

$C_{20}H_9N_2Cl_3$ 1:2:4-Trichloro-5:6:9′:10′-phenanthraphenazine, 576.
$C_{20}H_{10}N_2Cl_3$ 1:2:4-Trichloro-3-amino-5:6:9′:10′-phenanthraphenazine, 577.
$C_{20}H_{11}N_2Cl_3$ 1:4-Dichloro-2-amino-5:6:9′:10′-phenanthraphenazine, 577.
2:4-Dichloro-1-amino-5:6:9′:10′-phenanthraphenazine, 576.

$C_{20}H_{13}O_3N_3$ 6-Nitronaphthalene-1-azo-β-naphthol, 392.
$C_{20}H_{14}ON_2$ 2-Salicylideneaminoacridine, 460.
$C_{20}H_{16}O_6N_4$ 3′-Keto-4-methoxy-1:2-*cyclo*pentenonaphthalene 2:4-dinitrophenylhydrazone, 499.
$C_{20}H_{16}O_6N_4$ Furfurylidene-3-methoxyacetophenone 2:4-dinitrophenylhydrazone, 499.
$C_{20}H_{16}O_7N_2$ 3-Acetoxy-1-ethoxy-2-2′:4′-dinitrophenylnaphthalene, 69.
$C_{20}H_{17}O_2N_3$ 2-Carbethoxy-3-(3′-methyl-2′-quinoxalyl)indole, 400.
$C_{20}H_{17}O_2N_3$ 2-Carbethoxy-3-(2′-keto-1′-methyldihydro-3′-quinoxalyl)indole, 400.
8-β-Phthalimidoethyl-6-methoxyquinoline, 555.
$C_{20}H_{19}ON$ Phenylbenzyl-2-aminophenylcarbinol, 450.
$C_{20}H_{18}O_3N_2$ 2-*tert.*-Butyl-1:4-naphthaquinone *p*-nitrophenylhydrazone, 145.
$C_{20}H_{20}ON_2$ 2-*tert.*-Butyl-1:4-naphthaquinone phenylhydrazone, 145.
$C_{20}H_{20}O_3N_4$ Ethyl 3-methyl-4-quinazolonyl-2-pyruvate phenylhydrazone, 400.
$C_{20}H_{20}O_4N_2$ Ethyl oxaloacetate diphenylhydrazone, 660.
$C_{20}H_{20}O_7N_4$ Methyl 6-methoxy-5-methyl-1-tetralone-2-carboxylate 2:4-dinitrophenylhydrazone, 494.
$C_{20}H_{22}O_2N_2$ Phthalo-γ-(γ-phenoxypropylamino)propylimide, hydrobromide of, 555.
$C_{20}H_{23}ON_3$ 8-γ-Benzylaminopropylamino-6-methoxyquinoline, and its salts, 563.
$C_{20}H_{31}ON_3$ 8-ω-Aminodecylamino-6-methoxyquinoline, dihydrochloride, 558.
8-γ-*n*-Heptylaminopropylamino-6-methoxyquinoline, and its salts, 563.

### 20 IV

$C_{20}H_{13}O_5NS$ 1-Anilinoanthraquinone-3-sulphonic acid, salts, 46.
$C_{20}H_{14}O_2N_2S$ 1-Amino-4-anilinoanthraquinone-2-sulphonic acid, salts, 46.
$C_{20}H_{18}O_2N_2I$ [2-(3-Hydroxy-1-methylquinoxaline)][2-(1-methylbenzoxazole)]trimethincyanine iodide, 396.
$C_{20}H_{23}N_2IS_2$ [2-(3-Ethyldihydro-1:3-thiazine)][2-(3-ethyl-4:5-benzbenzthiazole)]methincyanine iodide, 247.
[2-(3-Ethyldihydro-1:3-thiazine)][2-(3-ethyl-6:7-benzbenzthiazole)]methincyanine iodide, 247.

## $C_{21}$ Group.

$C_{21}H_{16}N_2$ 5-Aminostyrylacridines, 7.
4-Phenyl-3-benzylcinnoline, 451.
$C_{21}H_{16}O$ Dicinnamylideneacetone, compounds of, with *s*-trinitrobenzene, 463.
$C_{21}H_{18}O_3$ Trimethylbenzoylnaphthoic acids, 240.
$C_{21}H_{19}N$ α-Phenyl-α-(2-aminophenyl)-β-benzylethylene, 451.
$C_{21}H_{20}O$ Trimethylbenzoyl-2-methylnaphthalenes, 240.
$C_{21}H_{20}O_3$ 4′-Methoxy-2-styryl-7-methyl-3-ethylchromone, 434.
$C_{21}H_{24}O_2$ 5-*o*-Hydroxybenzyl-12-methyl-1:2:3:4:12:13-hexahydroxanthen, 476.
$C_{21}H_{26}O_3$ 6″-Hydroxy-4″-*n*-amyloxy-2:2:5′-trimethyl-3′:4′:5′:6′-tetrahydrodibenzopyran, 286.

### 21 III

$C_{21}H_{13}O_4N_3$ 3-Nitro-5-*p*-nitrostyrylacridine, 347.
$C_{21}H_{14}O_3N_2$ α-(Nitrophenyl)-β-(5-acridyl)ethanols, 6.
5-Nitrostyrylacridines, 6.
2-Phenyl-6-pyridylquinoline-4-carboxylic acids, 412.
$C_{21}H_{15}O_3N_3$ α-(Nitrophenyl)-β-5-(3-nitroacridyl)ethanols, 347.
$C_{21}H_{16}ON_2$ 2-Keto-1-phenyl-3-benzyl-1:2-dihydroquinoxaline, 397.
$C_{21}H_{18}O_8N_4$ 5:5′-Dinitro-2:2′-dihydroxy-3:3′-bishydroxymethylbenzophenone phenylhydrazone, 321.
$C_{21}H_{16}N_2S$ 2-*p*-Dimethylaminostyryl*peri*naphtha-1:3-thiazine, 491.
$C_{21}H_{19}O_4N$ 4′-Nitro-2-styryl-7-methyl-3-*n*-propylchromone, 434.
$C_{21}H_{21}ON$ Phenyl-2-aminophenyl-β-phenylethylcarbinol, 450.
$C_{21}H_{21}O_2N$ 7-Methylnonadienynol α-naphthylurethanes, 267.
$C_{21}H_{22}O_4N_2$ Ethyl 1-quinolyl-2:5-dimethylpyrrole-3:4-dicarboxylates, 420.
$C_{21}H_{23}O_2N$ Decenynol α-naphthylurethanes, 265.
5-Ethyloct-5-en-7-yn-4-ol α-naphthylurethane, 264.
7-Methylnon-7-en-5-yn-4-ol β-naphthylurethane, 267.
$C_{21}H_{29}ON_3$ 8-ω-Cyanodecylamino-6-methoxyquinoline, 560.
$C_{21}H_{30}O_2N_2$ 8-ω-Carboxydecylamino-6-methoxyquinoline, 559.
$C_{21}H_{31}O_2N_3$ 8-ω-Carboxyamidodecylamino-6-methoxyquinoline, 560.
$C_{21}H_{31}O_4P$ Tetrahydrocannabinyl phosphate, 287.
$C_{21}H_{32}ON_4$ 8-ω-Guanyldecylamino-6-methoxyquinoline, and its hydrochloride, 560.
$C_{21}H_{37}O_2N$ Ethyl 1-*n*-decyl*cyclo*hexane-1-cyanoacetate, 502.

### 21 IV

$C_{21}H_{24}O_4N_4S$ 8-γ-*p*-Acetamidobenzenesulphonamidopropylamino-6-methoxyquinoline, 559.
$C_{21}H_{25}O_4N_2S$ [2-(3-Keto-1:4-dimethyldihydroquinoxaline)][(4-dimethylaminophenyl)]dimethincyanine sulphate, 396.
$C_{21}H_{26}O_6N_6S_2$ αβγ-Tri-(*p*-aminobenzenesulphonamido)propane, 609.
$C_{21}H_{28}O_{10}N_2S$ 6-Acetamido-4-tetra-acetyl-*d*-mannosidamino-2-methylthiopyrimidine, 573.
$C_{21}H_{29}O_3Cl_2P$ *O*-Dichlorophosphoryltetrahydrocannabinol, 287.

## $C_{22}$ Group.

$C_{22}H_{14}N_2$ 2-Phenyl-3:4:6:7-dibenzo-1:5-naphthyridine, and its picrate, 318.
$C_{22}H_{18}O_2$ 5:6:7:8-Tetramethyl-1:2-benzanthraquinone, 241.
$C_{22}H_{20}O_2$ 2-(2′:3′:4′:5′-Tetramethylbenzoyl)-1-naphthoic acid, 240.
$C_{22}H_{32}O_3$ 6″-Hydroxy-4″-*n*-hexyloxy-2:2:5′-trimethyl-3′:4′:5′:6′-tetrahydrodibenzopyran, 286.

### 22 III

$C_{22}H_{15}O_3N_3$ 3-*p*-Nitrobenzamido-2-phenylquinoline, 318.
$C_{22}H_{15}O_4N_3$ 3-Nitro-5-*p*-nitrostyryl-7-methylacridine, 347.

$C_{22}H_{16}ON_2$ Benzamidophenylquinolines, 317.
$C_{22}H_{17}ON_3$ Dibenzoylphenacylamine, 317.
$C_{22}H_{18}O_2N_2$ 2:3-Di-*p*-anisylquinoxaline, 612.
$C_{22}H_{19}O_5N_3$ 2-Nitro-5-benzyloxyphenylpyruvic acid phenylhydrazone, 49.
$C_{22}H_{19}N_2Cl$ 5-Aminostyrylacridine methochlorides, 7.
$C_{22}H_{20}N_3Cl$ 3-Amino-5-*p*-aminostyrylacridine methochloride, 347.
$C_{22}H_{21}O_4N$ 4′-Nitro-2-styryl-7-methyl-3-*n*-butylchromone, 435.
$C_{22}H_{21}N_4Cl$ 3:7-Diamino-5-*p*-aminostyrylacridine methochloride, 347.
$C_{22}H_{22}O_4N_2$ Ethyl 4-quinolyl-2:6-dimethylpyridine-3:5-dicarboxylates, 415.
$C_{22}H_{24}O_4N_2$ Ethyl 4-quinolyl-2:6-dimethyldihydropyridine-3:5-dicarboxylates, 414.
$C_{22}H_{24}O_5N_2$ Ethyl methoxyquinolyl-2:5-dimethylpyrrole-3:4-dicarboxylates, 420.
$C_{22}H_{27}ON_3$ 8-β′-Phenyl*iso*propyl-γ-aminopropylamino-6-methoxyquinoline, and its salts, 563.
$C_{22}H_{27}N_4Br$ ψ-6-Amino-2-*p*-dimethylaminostyryl-1-γ-aminopropylquinolinium bromide, hydrobromide o , 560.
$C_{22}H_{33}O_5N$ Delpheline, and its salts, 140.

**22 IV**

$C_{22}H_{20}ON_3I$ [2-(3-Keto-1-methyl-3:4-dihydroquinoxaline)][2-(1-methylquinoline)]trimethincyanine iodide, 396.
$C_{22}H_{21}O_3NS$ 5-Methylacridine metho-*p*-toluenesulphonate, 6.

**22 V**

$C_{22}H_{22}ON_3IS$ [2-(3-Hydroxy-1-ethylquinoxaline)][2-(1-ethylbenzthiazole)]trimethincyanine iodide, 396.

## $C_{23}$ Group.

$C_{23}H_{20}O_4$ Trimethylbenzoylnaphtho-acetoxylactones, 240.
$C_{23}H_{34}O_3$ 6″-Hydroxy-4″-*n*-heptyloxy-2:2:5′-trimethyl-3′:4′:5′:6′-tetrahydrodibenzopyran, 286.
$C_{23}H_{46}O_2$ *n*-Heptyl-*n*-tetradecylacetic acid, 618.
$C_{23}H_{48}O$ 3-Decyltridecanol, 619.
Methyl-*n*-nonyl-*n*-dodecylcarbinol, 618.

**23 III**

$C_{23}H_{16}O_2N_4$ 3-(2-Keto-1-phenyldihydroquinoxalyl)-3-(2-ketodihydroquinoxalyl)methane, 400.
$C_{23}H_{16}O_3N_2$ 3-Benzamido-2-phenylquinoline-4-carboxylic acid, 318.
$C_{23}H_{16}O_5N_4$ 3-Nitro-7-acetamido-5-*p*-nitrostyrylacridine, 347.
$C_{23}H_{17}O_3N_3$ 1-Benzamido-6:17-diketo-6:8:15:17-tetrahydro-7:16-diazanaphthacene, 659.
$C_{23}H_{17}O_4N_5$ 6-Nitro-4-*p*-tolueneazonaphthalene-1-azoresorcinol, 393.
$C_{23}H_{18}ON_2$ 5-*m*-Acetamidostyrylacridine, 7.
$C_{23}H_{18}ON_4$ *s*-Bis-α-4-pyridylphenylurea, 413.
$C_{23}H_{18}O_2N_2$ 2:4-Diphenylpyrrole-5-aldehyde *p*-nitrophenylhydrazone, 597.
$C_{23}H_{18}N_2S_2$ Trimethin[2-(3-ethyldihydrobenzthiazole)][2-(*peri*naphtha-1:3-thiazine)], 490.
$C_{23}H_{21}O_2N$ Phenyl-2-benzamidophenylallylcarbinol, 451.
$C_{23}H_{22}O_4N_4$ [Bis-2-(3-hydroxy-1-methylquinoxaline)]trimethincyanine acetate, 396.
$C_{23}H_{23}O_2N$ Phenyl-2-acetamidophenyl-β-phenylethylcarbinol, 451.
$C_{23}H_{23}O_4N$ 4′-Nitro-2-styryl-7-methyl-3-*n*-amylchromone, 435.
$C_{23}H_{24}O_2N_2$ 8-ω-Carbethoxydecylamino-6-methoxyquinoline, 560.
$C_{23}H_{33}ON_4$ 8-ω-Aminodecyl-γ-aminopropylamino-6-methoxyquinoline, and its meconate, 559.

**23 IV**

$C_{23}H_{12}O_4N_4Cl_4$ 2:3:5:6-Tetrachloro-4-nitrobenzeneazo-2′-hydroxy-3′-naphthanilide, 234.
$C_{23}H_{13}O_5N_4Cl_3$ 2:3:5-Trichloro-4-nitro-6-hydroxybenzeneazo-2′-hydroxy-3′-naphthanilide, 237.
$C_{23}H_{16}ON_2S$ Trimethin[2-(3-ethyldihydrobenzoxazole)][2-(*peri*naphtha-1:3-thiazine)], and its hydrochloride, 490.
$C_{23}H_{23}O_2ClAs$ 2-Phenyl-2-*p*-chloro-1:2:3:4-tetrahydro*iso*arsinolinium hydroxide, salts of, 553.
$C_{23}H_{22}O_3N_2Br$ ψ-6-Acetamido-2-methyl-1-γ-phthalimidopropylquinolinium bromide, 560.
$C_{23}H_{24}ON_2I$ [2-(3-Keto-1-methyl-3:4-dihydroquinoxaline)][2-(1:3:3-trimethylindoline)]trimethincyanine iodide, 396.

**23 V**

$C_{23}H_{13}O_3N_3Cl_3Br$ 2:3:5-Trichloro-4-bromo-6-hydroxybenzeneazo-2′-hydroxy-3′-naphthanilide, 237.
$C_{23}H_{21}OClBrAs$ *dl*-2-Phenyl-2-*p*-chlorophenacyl-1:2:3:4-tetrahydro*iso*arsinolinium bromide, preparation and resolution of, 550.
$C_{23}H_{21}OClIAs$ *dl*-2-Phenyl-2-*p*-chlorophenacyl-1:2:3:4-tetrahydro*iso*arsinolinium iodide, 553.
$C_{23}H_{24}ON_2IS$ [2-(3-Keto-4-methyl-1-ethyldihydroquinoxaline)][2-(1-ethylbenzthiazole)]trimethincyanine iodide, 397.

## $C_{24}$ Group.

$C_{24}H_{16}$ 2-Phenylchrysene, 450.
Tetraphenylene, 326.

**24 II**

$C_{24}H_{15}Br$ Bromotetraphenylene, 327.
$C_{24}H_{16}N_2$ 4-Phenyl-3-(1′-naphthyl)cinnoline, 450.
$C_{24}H_{19}N$ α-Phenyl-α-(2-aminophenyl)-β-(1′-naphthyl)ethylenes, 449.
$C_{24}H_{24}O_2$ β-Phenyl-αα-di-(*p*-ethoxyphenyl)ethylene, 394.
$C_{24}H_{26}O_2$ Di-(*p*-ethoxyphenyl)benzylcarbinol, 394.
$C_{24}H_{30}O$ α-(2:2-Dimethylchromanyl-3)-β-(2:3-dimethylchromanyl-2)-ethane, 476.
$C_{24}H_{46}O_2$ Methyl-*n*-heptyl-*n*-tetradecylacetic acid, 618.

### 24 III

$C_{24}H_{12}O_8N_4$ Tetranitrotetraphenylene, 327.
$C_{24}H_{17}O_4N_3$ α-(2:4-Dinitrophenyl)-β-(2:4-diphenyl-5-pyrrolyl)ethylene, 597.
$C_{24}H_{18}O_2N_4$ 3-(2-Keto-1-methyldihydroquinoxalyl)-3-(2-keto-1-phenyldihydroquinoxalyl)methane, 400.
2-(3-Methyl-4-quinazolonyl)-3-(2-keto-1-phenyldihydroquinoxalyl)methane, 400.
$C_{24}H_{21}ON_3$ [2-(3-Keto-4-phenyl-1-methyldihydroquinoxaline)][(4-dimethylaminophenyl)]dimethincyanine, 397.
$C_{24}H_{23}O_2Br$ β-Bromo-β-phenyl-αα-di-(*p*-ethoxyphenyl)ethylene, 394.
$C_{24}H_{23}N_2Cl$ 5-*p*-Dimethylaminostyrylacridine methochloride, 7.
$C_{24}H_{24}O_4N_2$ Deca-3:7-dien-5-yn-2:9-diol bisphenylurethane, 269.
$C_{24}H_{26}O_3N_4$ 8-γ-Phthalimidopropyl-γ-aminopropylamino-6-methoxyquinoline, dihydrobromide of, 556.
$C_{24}H_{32}O_4N_2$ Decane-2:9-diol bisphenylurethane, 269.

### 24 IV

$C_{24}H_{15}O_5N_4Cl_3$ 2:3:5-Trichloro-4-nitro-6-methoxybenzeneazo-2′-hydroxy-3′-naphthanilide, 237.
$C_{24}H_{19}O_2N_4Cl$ 3-(2-Keto-1-methyldihydroquinoxalyl)-3-(2-keto-1-phenyldihydroquinoxalyl)methane hydrochloride, 400.
$C_{24}H_{20}O_6N_2S_2$ 6-Nitrodi-*p*-toluenesulphon-1-naphthalide, 391.
$C_{24}H_{20}N_3IS$ [2-(1-Methylbenzthiazole)][2-(1-phenyl-3-methylquinoxaline)]methincyanine iodide, 399.
$C_{24}H_{22}O_4N_2S_2$ *NN′*-Ditoluene-*p*-sulphonyl-1:4-naphthylenediamine, 636.
$C_{24}H_{24}O_4N_2S$ 3-Acetamido-5-methylacridine metho-*p*-toluenesulphonate, 346.
$C_{24}H_{25}ON_3Cl$ [2-(3-Keto-1:4-dimethyldihydroquinoxaline)][2-(1:3:3-trimethylindoline)]trimethincyanine chloride, 396.
$C_{24}H_{26}O_6N_4S$ [3-Bis-(3-keto-1:4-dimethyldihydroquinoxaline)]trimethincyanine sulphate, 396.
$C_{24}H_{33}O_6N_7S_3$ Tri-(β-*p*-aminobenzenesulphonamidoethyl)amine, 608.

### 24 V

$C_{24}H_{21}ON_2IS$ [2-(3-Ethylbenzoxazole)][2-(3-methyl*peri*naphtha-1:3-thiazine)]trimethincyanine iodide, 490.

## $C_{25}$ Group.

$C_{25}H_{17}N_3$ 2:3-Diphenyl-6-α-pyridylquinoxaline, 405.
6-β-Pyridyl-2:3-diphenylquinoxaline, 413.
$C_{25}H_{34}N_2$ 5-Dodecylaminoacridine, and its hydrochloride, 654.
$C_{25}H_{46}O_2$ Ethyl 3-decyl-$\Delta^2$-tridecenoate, 619.
$C_{25}H_{50}O_2$ β-*n*-Decyl-β-*n*-dodecylpropionic acid, 618.
Ethyl 3-decyltridecoate, 619.
Methyl-*n*-decyl-*n*-dodecylacetic acid, 617.
3-Methyl-2-*n*-dodecyl-lauric acid, 618.

### 25 III

$C_{25}H_{21}O_2N_3$ 3-Acetamido-5-*p*-acetamidostyrylacridine, 347.
$C_{25}H_{39}O_2N$ Lycoctonine, 141.
$C_{25}H_{51}ON$ Methyldecyldodecylacetamide, 617.

### 25 IV

$C_{25}H_{21}O_3N_2S$ *NN′*-Diphenylbenzamidine *p*-nitrobenzenesulphonate, 103.
$C_{25}H_{24}ON_3Cl$ [2-(3-Keto-4-phenyl-1-methyldihydroquinoxaline)][(4-dimethylaminophenyl)]dimethincyanine chloride, 397.
$C_{25}H_{40}ON_3Cl$ 5-Chloro-8-ω-diethylaminoundecylamino-6-methoxyquinoline, hydrochloride of, 559.

### 25 V

$C_{25}H_{23}ON_2IS$ [2-(3-Ethylbenzoxazole)][2-(3-ethyl*peri*naphtha-1:3-thiazine)]trimethincyanine iodide, 491.

## $C_{26}$ Group.

$C_{26}H_{22}O_3$ 4′-Methoxy-2-styryl-3-benzyl-7-methylchromone, 435.
$C_{26}H_{44}O_3$ β-Phenyl-ααβ-trimethyl-*n*-butyric anhydride, 429.
$C_{26}H_{52}O_2$ Ethyl-*n*-decyl-*n*-dodecylacetic acid, 618.
β-Methyl-β-*n*-decyl-β-*n*-dodecylpropionic acid, 618.
2-Methyl-5-decylpentadecoic acid, 619.
4-Methyl-3-*n*-dodecyltridecoic acid, 618.

### 26 III

$C_{26}H_{23}O_2N_3$ 3-Acetamido-5-*p*-acetamidostyryl-7-methylacridine methochloride, 347.
$C_{26}H_{22}N_2Cl$ *p*-Chloro-(αβ-bis-*p*-tolylethylamino)vinylbenzene, 67.
$C_{26}H_{53}ON$ Ethyl-*n*-decyl-*n*-dodecylacetamide, 618.
$C_{26}H_{53}ON$ β-Methyl-β-*n*-decyl-β-*n*-dodecylpropionamide, 618.

### 26 IV

$C_{26}H_{16}O_8N_2S$ 1:4-Dianilinoanthraquinone-2-sulphonic acid, salts, 46.
$C_{26}H_{20}O_7N_4S$ Aniline 1-diazophenylaminoanthraquinone-2-sulphonate, 46.

### 26 V

$C_{26}H_{23}ON_3ClS$ [2-(3-Keto-4-phenyl-1-methyl-3:4-dihydroquinoxaline)][2-(1-methylbenzthiazole)]trimethincyanine chloride, 397.
$C_{26}H_{29}O_2N_4Cl_2S$ Bis-(8-γ-chloropropylamino-6-methoxy-5-quinolyl) sulphide, and its hydrochloride, 562.

## $C_{27}$ Group.

$C_{27}H_{44}O$ $\Delta^4$-Cholestenone, 602.
$C_{27}H_{46}O_2$ $\beta$-Cholesterol oxide, 613.
$C_{27}H_{54}O_2$ Methyl $\beta$-methyl-$\beta$-decyl-$\beta$-dodecylpropionate, 618.

### 27 III

$C_{27}H_{20}O_2N_2$ 1-Anilino-4-*p*-toluidinoanthraquinone, 47.
$C_{27}H_{20}N_2S_2$ Trimethin[2-(3-ethyldihydrobenzbenzthiazole)][2-(*peri*naphtha-1:3-thiazines)], 490.
$O_{27}H_{24}O_2N_4$ 3:7-Bis(acetamido)-5-*p*-acetamidostyrylacridine, 347.
$C_{27}H_{44}O_3S$ *cis*-$\Delta^5$-Cholestene-3:4-diol *endo*sulphite, 139.

### 27 IV

$C_{27}H_{20}ON_2S$ Trimethin[2-(3-ethyldihydrobenzbenzoxazole)][2-(*peri*naphtha-1:3-thiazines)], 490.
$C_{27}H_{20}O_5N_2S$ 4-Anilino-1-*p*-toluidinoanthraquinone-2-sulphonic acid, salts, 47.
$C_{27}H_{21}N_2IS_2$ Bis-2-(3-methyl*peri*naphtha-1:3-thiazine)trimethincyanine iodide, 489.
$C_{27}H_{25}O_3N_4Cl$ 2-Chloro-5-(6′-methoxyquinolyl-8′-$\gamma$-aminopropylamino)-7-methoxyacridine, and its dihydrochloride, 556.
$C_{27}H_{32}O_6N_6S_3$ $\alpha\beta\gamma$-Tri-(*p*-acetamidobenzenesulphonamido)propane, 608.

## $C_{28}$ Group.

$C_{28}H_{22}O_4$ Trimethylbenzoyl-1-naphthobenzoyloxy-lactone, 240.

### 28 III

$C_{28}H_{16}O_4N_2$ 4:4′-Diamino-1:1′-dianthraquinonyl, 47.
$C_{28}H_{22}O_2N_2$ 1-Anilino-4-*m*-4′-xylidinoanthraquinone, 47.
$C_{28}H_{32}O_3N_2$ 8-$\omega$-Phthalimidodecylamino-6-methoxyquinoline, and its hydrochloride, 558.

### 28 IV

$C_{28}H_{14}O_4N_2Br_2$ 2:2′-Dibromo-4:4′-diamino-1:1′-dianthraquinonyl, 47.
$C_{28}H_{16}O_{10}N_2S_2$ 4:4′-Diamino-1:1′-dianthraquinonyl-3:3′-disulphonic acid, salts, 47.
$C_{28}H_{22}ON_2Cl_2$ Di-($\beta$-phenylamino-$\alpha$-*p*-chlorophenylvinyl) ether, 65.
$C_{28}H_{23}O_5N_2S$ 4-Anilino-1-*m*-4′-xylidinoanthraquinone-2-sulphonic acid, salts, 47.
$C_{28}H_{24}O_4N_2S_2$ Bis-2-(3-methyl*peri*naphtha-1:3-thiazine)trimethincyanine methyl sulphate, 489.
$C_{28}H_{42}N_2$ 5-Hexadecylaminoacridine, and its hydrochloride, 654.

## $C_{29}$ Group.

$C_{29}H_{48}O_3$ 4-Acetoxy-$\Delta^5$-cholesten-3-ol, 137.
$C_{29}H_{48}O_4$ 3-*O*-Carbomethoxy-4-hydroxycholesterol, 439.

### 29 III

$C_{29}H_{47}O_2Cl$ 4-Chloro-3-acetoxy-$\Delta^5$-cholestene, 138.

### 29 IV

$C_{29}H_{29}N_2IS_2$ Bis-2-(3-methyl*peri*naphtha-1:3-thiazine)pentamethincyanine iodide, 489.
$C_{29}H_{25}N_2IS_2$ Bis-2-(3-ethyl*peri*naphtha-1:3-thiazine)trimethincyanine iodide, 489.
$C_{29}H_{27}O_5N_3S$ [2-(3-Keto-4-phenyl-1-methyl-3:4-dihydroquinoxaline)][2-(1-methylquinoline)]trimethincyanine sulphate, 397.
$C_{29}H_{28}ON_2Cl$ [2-(3-Keto-4-phenyl-1-methyl-3:4-dihydroquinoxaline)][2-(1:3:3-trimethylindoline)]trimethincyanine chloride, 397.
$C_{29}H_{34}O_6N_6S_4$ Tetra-(*p*-aminobenzenesulphonamidomethyl)methane, 608.

## $C_{30}$ Group.

$C_{30}H_{48}O_4$ Melanthigenin, constitution of, 70.
$C_{30}H_{50}O_3$ 4-Propionoxy-$\Delta^5$-cholesten-3-ol, 138.
$C_{30}H_{50}O_4$ 3-*O*-Carbethoxy-4-hydroxycholesterol, 440.
$C_{30}H_{58}O_4$ Ethyl (3-decyltridecyl)malonate, 619.
Ethyl *sec.*-undecyl-*n*-dodecylmalonate, 618.

### 30 III

$C_{30}H_{12}O_{12}N_2$ Dinitro-2:2′-dianthraquinonyl-1:1′-dicarboxylic acid, 32.
$C_{30}H_{52}ON_4$ 8-$\omega$-Aminodecyl-$\omega$-aminodecylaminodecylamino-6-methoxyquinoline, and its meconate, 558.

### 30 IV

$C_{30}H_{38}O_6N_6S_4$ Tetra-(*p*-aminobenzenesulphonamidoethyl)ethylenediamine, 609.
$C_{30}H_{39}O_6N_7S_3$ Tri-($\beta$-*p*-acetamidobenzenesulphonamidoethyl)amine, 608.

## $C_{31}$ Group.

$C_{31}H_{50}O_3$ 4-Butyroxy-$\Delta^5$-cholesten-3-ol, 138.
$C_{31}H_{46}O_3$ Nor-$\alpha$-amyradiononyl acetate, 524.
$C_{31}H_{50}O_5$ 3-*O*-Carbomethoxy-4-acetoxycholesterol, 439.

## $C_{32}$ Group.

$C_{32}H_{18}O_6$ Methyl 2:2′-dianthraquinonyl-1:1′-dicarboxylate, 32.
$C_{32}H_{22}N_2$ 2:2′:4:4′-Tetraphenylazadipyrromethine, and its metallic complexes, 592.
$C_{32}H_{26}O_4$ Dienœstrol dibenzoate, 612.
$C_{32}H_{28}O_5$ γγ-Bis-4-hydroxyphenylhexan-δ-one dibenzoate, 612.
$C_{32}H_{30}O_2$ Dienœstrol dibenzyl ether, 612.
$C_{32}H_{30}O_6$ γδ-Bis-4-hydroxyphenylhexane-γδ-diol dibenzoate, 611.
$C_{32}H_{48}O_5$ Ketoacetylursolic acid, 524.
$C_{32}H_{50}O_4$ Acetylursolic acid, oxidation of, 523.
$C_{32}H_{52}O_4$ 3-Acetoxy-4-propionoxy-$\Delta^5$-cholestene, 138.
$C_{32}H_{52}O_5$ 3-*O*-Carbethoxy-6-acetoxy-$\Delta^4$-cholesten-3-ol, 440.
3-*O*-Carbethoxy-4-acetoxycholesterol, 440.

### 32 III

$C_{32}H_{16}O_{12}N_2$ Methyl dinitro-2:2′-dianthraquinonyl-1:1′-dicarboxylate, 32.
$C_{32}H_{21}O_6N_5$ 2:2′-Diphenyl-4:4′-di-(*m*-nitrophenyl)azadipyrromethine, 592.
$C_{32}H_{28}O_4N_4$ 8-Di-γ-phthalimidopropylamino-6-methoxyquinoline, and its hydrobromide, 556.
$C_{32}H_{30}O_6S_2$ Dienœstrol ditoluene-*p*-sulphonate, 612.
$C_{32}H_{33}O_2N_3$ 2:2′-Diphenyl-4:4′-di-(*m*-hydroxyphenyl)azadipyrromethine, 593.
$C_{32}H_{34}O_6S_2$ γδ-Bis-4-hydroxyphenylhexane-γδ-diol ditoluene-*p*-sulphonate, 611.
$C_{32}H_{44}O_8N_2$ Anthranoyl-lycoctonine, 141.

### 32 IV

$C_{32}H_{26}O_2N_2Cl_2$ Diacetyl-di-(β-phenylamino-α-*p*-chlorophenylvinyl) ether, 65.
$C_{32}H_{31}O_2N_4Br$ ψ-6-Acetamido-2-*p*-dimethylaminostyryl-1-γ-phthalimidopropylquinolinium bromide, 560.

## $C_{33}$ Group.

$C_{33}H_{24}N_2$ 2:2′:4:4′-Tetraphenyldipyrromethine, and its copper complex, 597.
$C_{33}H_{36}O_{12}$ Hexa-acetoxy-3:3:3′:3′-tetramethylbis-1:1′-*spiro*hydrindenes, 486.
$C_{33}H_{54}O_4$ 3-Acetoxy-4-butyroxy-$\Delta^5$-cholestene, 138.

### 33 III

$C_{33}H_{25}ON_3$ 2:2′:4-Triphenyl-4′-*p*-anisylazadipyrromethine, 595.

## $C_{34}$ Group.

$C_{34}H_{29}N_3$ *NN*-Di-(β-phenylamino-α-phenylvinyl)aniline, 64.
$C_{34}H_{50}O_3$ 4-Benzoyloxy-$\Delta^5$-cholesten-3-ol, 138.
β-Cholesterol benzoate, 614.
$C_{34}H_{52}O_5$ Ethyl ketoacetylursolate, 524.

### 34 III

$C_{34}H_{14}O_6N_2$ Dinitrodibenzanthrone, 31.
$C_{34}H_{25}ON_3$ 2:2′:4-Triphenyl-4′-*p*-anisyldipyrromethine, 597.
$C_{34}H_{20}O_{12}N_2$ Ethyl dinitro-2:2′-dianthraquinonyl-1:1′-dicarboxylate, 32.
$C_{34}H_{23}O_4N_3$ 2:2′-Diphenyl-4:4′-di-(3:4-methylenedioxyphenyl)azadipyrromethine, 593.
$C_{34}H_{27}O_2N_3$ 2:2′-Di-*p*-anisyl-4:4′-diphenylazadipyrromethine, 593.
2:2′-Diphenyl-4:4′-di-*p*-anisylazadipyrromethine, 593.
$C_{34}H_{27}N_3Cl_2$ *NN*-Di-(β-phenylamino-α-*p*-chlorophenylvinyl)aniline, 66.
$C_{34}H_{49}O_2Cl$ 4-Chloro-3-benzoyloxy-$\Delta^5$-cholestene, 139.

### 34 IV

$C_{34}H_{30}O_6N_6S$ [Bis-2-(3-keto-4-phenyl-1-methyldihydroquinoxaline)]trimethincyanine sulphate, 397.
$C_{34}H_{46}O_2N_6S$ Bis-(8-γ-diethylaminopropylamino-6-methoxy-5-quinolyl) sulphide, and its hydrochloride, 562.

## $C_{35}$ Group.

$C_{35}H_{27}O_4N_4Cl$ 2-Chloro-5-γ-phthaliminopropylamino-(*N*-6′-methoxy-8′-quinolyl)-7-methoxyacridine, 556.

## $C_{36}$ Group.

$C_{36}H_{31}N_5$ 2:2′-Diphenyl-4:4′-di-(*p*-dimethylaminophenyl)azadipyrromethine, 593.
$C_{36}H_{52}O_5$ 3-*O*-Carbomethoxy-4-benzoyloxycholesterol, 435.

### 36 III

$C_{36}H_{29}O_2N_5$ 2:2′-Diphenyl-4:4′-di-(*p*-acetamidophenyl)azadipyrromethine, 593.
$C_{36}H_{31}O_4N_3$ 2:2′:4:4′-Tetra-*p*-anisylazadipyrromethine, 593.
$C_{36}H_{53}O_4Cl$ 5-Chloro-3-acetoxy-6-benzoyloxycholestane, 614.

## $C_{37}$ Group.

$C_{37}H_{31}N_3$ *NN*-Di-(β-*p*-tolylamino-α-phenylvinyl)-*p*-toluidine, 64.
$C_{37}H_{54}O_5$ 3-*O*-Carbethoxy-4-benzoyloxycholesterol, 440.

### 37 III

$C_{37}H_{45}O_{10}N_2$ Methyl-lycaconitine, and its hydriodide, 140.

### 37 IV

$C_{37}H_{44}O_{12}N_6S_4$ Tetra-(*p*-acetamidobenzenesulphonamidomethyl)methane, 608.

## $C_{38}$ Group.

$C_{38}H_{39}N_3I_2$ 2:2′-Diphenyl-4:4′-di-(*p*-dimethylaminophenyl)azadipyrromethine dimethiodide, 593.

### 38 IV

$C_{38}H_{46}O_{12}N_6S_4$ Tetra-(*p*-acetamidobenzenesulphonamidoethyl)ethylenediamine, 609.
$C_{38}H_{28}N_2$ 2:2′:4:4′-Tetraphenyl-*meso*-phenyldipyrromethine, and its copper complex, 597.

## $C_{53}$ Group.

$C_{53}H_{36}N_4$ 3:3′-Dibenzylideneamino-2:2′:4:4′-tetraphenyl-*meso*-phenyldipyrromethine, 598.

### 53 III

$C_{53}H_{38}O_2N_4$ 3:3′-Dibenzamido-2:2′:4:4′-tetraphenyl-*meso*-phenyldipyrromethine, 599.

## $C_{56}$ Group.

$C_{56}H_{42}O_3N_4$ 3:3′-(Di-*p*-anisylideneamino)-2:2′:4:4′-tetraphenyl-*meso*-*p*-anisyldipyrromethine, 598.

## $C_{58}$ Group.

$C_{58}H_{94}O_7S$ Bis-(4:4′-acetoxycholesteryl) sulphite, 139.

# SYMBOLS FOR THERMODYNAMICAL AND PHYSICO-CHEMICAL QUANTITIES AND CONVENTIONS RELATING TO THEIR USE, ADOPTED AS RECOMMENDED PRACTICE BY THE CHEMICAL SOCIETY.

*(Where two or more symbols separated by commas or semicolons are given for a quantity, these symbols are to be regarded as alternatives for which no preference is expressed. On the other hand, where two symbols are separated by a dotted line, the former is the first preference.)*

## 1. To be Printed in Black Italic.

*(Certain important physical constants.)*

***F*** Faraday's constant.
***J*** Mechanical equivalent of heat.
***N*** Avogadro's number.
***R*** Gas constant per mol. / Rydberg's constant.
***c*** Velocity of light in vacuo.
***e*** Electronic charge (charge equal and opposite in sign to that of an electron).
***g*** Acceleration due to gravity (standard value, if variation from standard is significant).
***h*** Planck's constant.
***k*** Boltzmann's constant.
***m*** Rest mass of an electron.

## 2. To be Printed in Ordinary Italic, when not Greek.

*General Physics and Chemistry.*

| | |
|---|---|
| Length | $l$ |
| mean free path of molecules | $l$ |
| height | $h$ |
| diameter, distance | $d$ |
| diameter of molecules | $\sigma$ |
| radius | $r$ |
| Mass | $m$ |
| molecular weight | $M$ |
| atomic weight | $A$ |
| atomic number | $Z$ |
| gram-equivalent weight | $Z, J$ |
| Time | $t$ |
| time interval, especially half- or mean-life | $\tau$ |
| frequency | $\nu$ |
| Velocity | $v$; $c$, $(u, v, w)$ |
| of ions | $u$ (with subscript) |
| angular | $\omega$ |
| Acceleration | $f \ldots a$ |
| due to gravity (as variable) | $g$ |
| Force | $F$, $(X, Y, Z)$ |
| Moment of inertia | $I$ |
| Pressure | $p, P$ |
| especially osmotic | $\Pi$ |
| Volume | $v, V$ |
| Density | $\rho \ldots d$ |
| Compressibility | $\kappa \ldots K$ |

| | |
|---|---|
| Viscosity | $\eta$ |
| Fluidity | $\phi$ |
| Surface area | $A \ldots s$ |
| Angle of contact | $\theta$ |
| Surface tension | $\gamma \ldots \sigma$ |
| Parachor | $[P]$ |
| Surface concentration excess | $\Gamma$ |
| Number of mols | $n$ |
| Concentration, mol fraction | $N, x$ |
| in other terms | $c, C$ |
| Solubility | $s$ |
| Diffusion coefficient | $D$ |
| Chemical equilibrium constant (products/reactants) | $K$ |
| solubility product | $K_s \ldots L$ |
| Velocity constant of chemical reaction | $k$ |
| Number of molecular collisions per second | $Z$ |
| Partition function | $f$ |
| Efficiency, of any process | $\eta$ |
| Wave function | $\psi$ |

*Heat and Thermodynamics.*

| | |
|---|---|
| Temperature, on absolute scale, (°K) | $T$ |
| on other scales | $\theta \ldots t$ |
| Thermal conductivity | $k$ |
| Energy (general symbol) | $E$ |
| Work done by or on a system | $w \ldots W$ |
| Heat entering a system | $q$ |
| Specific heat | $c_p$ and $c_v$ |
| molecular heat | $C_p$ and $C$ |
| Ratio of specific heats | $\gamma$ |
| Latent heat, per g. | $l$ |
| per mol | $L$ |
| Intrinsic energy | $U \ldots E$ |
| Enthalpy, total heat, or heat content | $H$ |
| Entropy | $S$ |
| Free energy (Helmholtz) | $A \ldots F$ |
| Thermodynamic potential, Gibbs function, free energy (G. N. Lewis) | $G$ |
| Vapour pressure constant | $i$ |
| Chemical potential | $\mu$ |
| Activity | $a$ |
| coefficient (for molar concentration) | $f$ |
| Osmotic coefficient | $g$ |
| Van 't Hoff's factor | $i$ |

*Electricity.*

| | |
|---|---|
| Quantity of electricity | $Q$ |
| especially electrostatic charge | $e$ |
| Potential (difference) | $V$ |
| Volta potential | $V$ |
| electrokinetic potential | $\zeta$ |
| especially electromotive force of voltaic cells | $E$ |
| Potential gradient, in electric field | $X$ |
| Electronic exit work function | $\phi$ |

| | |
|---|---|
| Current | $I$ |
| Resistance | $R$ |
| specific resistance | $\rho \ldots r$ |
| specific conductance | $\kappa \ldots \sigma$ |
| Inductance, self | $L$ |
| mutual | $M$ |
| Electrostatic capacity | $C$ |
| Dielectric constant | $\epsilon$ |
| Dipole moment | $\mu$ |

*Electrochemistry.*

| | |
|---|---|
| Degree of electrolytic dissociation | $\alpha$ |
| Valency of an ion | $z$ |
| Ionic strength | $I$ |
| Equivalent conductance | $\Lambda$ |
| equivalent ionic conductance, "mobility" | $l$ (with subscript) |
| Transport number | $T$ (with subscript) . . . $n$ (with subscript) |
| Single electrode potential | $e$ (with subscript), $E$ (with subscript) |
| Electrolytic polarisation, overvoltage | $\eta \ldots \pi$ |

*Magnetism.*

| | |
|---|---|
| Magnetic field strength | $H$ |
| flux | $\phi$ |
| permeability | $\mu$ |
| susceptibility—volume | $\kappa$ |
| mass | $\chi$ |
| moment | $M$ |
| induction | $B$ |

*Optics.*

| | |
|---|---|
| Wave length | $\lambda$ |
| Wave number | $\nu$ |
| Intensity of light | $I$ |
| Refractive index | $n$ (with subscript) . . . $\mu$ (with subscript) |
| specific refraction | $r$ (with subscript) |
| molecular refraction | $[R]$ (with subscript) |
| Molar extinction coefficient | $\epsilon$ |
| Angle of (optical) rotation | $\alpha$ |
| specific rotation | $[\alpha]$ |
| Specific magnetic rotation | $\omega$ |

**3. To be Printed in Roman, when not Greek.**

(a) *Examples of Mathematical Constants and Operators.*

| | |
|---|---|
| Base of natural logarithms | e |
| Ratio of circumference to diameter | $\pi$ |
| Differential | d |
| partial | $\partial$ |
| Increment | $\Delta$ |
| very small increment | $\delta$ |
| Sum | $\Sigma$ |
| Product | $\Pi$ |
| Function | f, $\phi$ |

(b) *Examples of single-letter abbreviations.*

| | |
|---|---|
| *Ampère (in sub-units) | a. |
| Volt | v. |
| Ohm | Ω. |
| Watt | w. |
| Farad | f. |
| Henry | h. |
| Centigrade | c. |
| Fahrenheit | f. |
| Kelvin | k. |
| Ångstrom unit | a. |
| micron | μ. |
| metre | m. |
| gram | g. |
| litre | l. |
| Röntgen unit | r. |
| †Normal (concentration) | n. |
| †Molar (concentration) | m. |

The following prefixes to abbreviations for the names of units should be used to indicate the specified multiples or sub-multiples of these units:

| | | |
|---|---|---|
| M | mega- | $10^{6}\times$ |
| k | kilo- | $10^{3}\times$ |
| d | deci- | $10^{-1}\times$ |
| c | centi- | $10^{-2}\times$ |
| m | milli- | $10^{-3}\times$ |
| μ | micro- | $10^{-6}\times$ |

*e.g.*, MΩ. denotes megohm; kw., kilowatt; and μg., microgram. The use of μμ. instead of mμ. to denote $10^{-7}$ cm., or of γ to denote microgram is deprecated.

## 4. Subscripts and other Modifying Signs.

(a) *Subscripts to symbols for quantities.*

| | |
|---|---|
| I, II . . . | *especially with symbols for thermodynamic functions,* referring to different systems or different states of a system. |
| 1, 2 . . . | |
| A, B . . . | referring to molecular species A, B, etc. |
| i | referring to a typical ionic species i. |
| u | referring to an undissociated molecule. |
| +, − | referring to a positive or negative ion, or to a positive or negative electrode. |
| $p$, $v$, $T$ | indicating constant pressure, volume, and temperature respectively. |
| $q$ | indicating adiabatic conditions. |
| $w$ | indicating that no work is performed. |
| $p$, $c$, $a$ | *with symbol for an equilibrium constant,* indicating that it is expressed in terms of pressure, concentration, or activity. |
| G, V, L, X | referring to gas, vapour, liquid, and crystalline states, respectively. |
| f, e, s, t, d | referring to fusion, evaporation (vaporisation of liquid), sublimation, transition, and dissolution or dilution respectively. |
| c | referring to the critical state or indicating a critical value. |
| 0 | referring to a standard state, or indicating limiting value at infinite dilution. |

* *E.g.* "ma." for "milliampère"; but "amp." is preferred for "ampère."

† Separated by a hyphen (and no full stop) from a chemical formula which follows it.

$_{C, D, \nu}$ *with symbols for optical properties,* referring to a particular wavelength.

Where a subscript has to be added to a symbol which already carries a subscript, the two subscripts may be separated by a comma or the symbol with the first subscript may be enclosed in parentheses with the second subscript outside.

(b) *Other modifying signs.*

° *as right-hand superscript to symbol (particularly to a symbol for a general thermodynamic function—see p. 5),* referring to a standard state.

[ ] *enclosing formula of chemical substance,* indicating its molar concentration.

{ } *enclosing formula of chemical substance,* indicating its molar activity.

In crystallography it is recommended that:

Millerian indices be enclosed in parentheses, ( );
Laue indices be unenclosed;
Indices of a plane family be enclosed in braces, { };
Indices of a zone axis or line be enclosed in brackets, [ ].

Numerals attached to a symbol for a chemical element in various positions have the following meanings:

upper left mass number of atom.
lower left nuclear charge of atom.
lower right number of atoms in molecule.

*e.g.*, $^{7}_{3}Li$; $^{2}_{1}H_{2}$ (= $D_2$).

## ALPHABETICAL INDEX OF RECOMMENDED SYMBOLS, and single-letter abbreviations.

including all those given in the above lists except prefixes, subscripts and other modifying signs.

*The name of any quantity for which a given symbol is a second preference is printed in parentheses.*

*A* free energy—Helmholtz; atomic weight; surface area.
A. Ångstrom unit.
*a* activity; (acceleration).
a. ampère, in sub-units—see footnote, p. 2093.
*B* magnetic induction.
*C* concentration; electrostatic capacity.
*with subscript:* molecular heat capacity.
c. Centigrade.
*c* velocity of light in vacuo.
*c* velocity; concentration.
*with subscript:* specific heat.
*D* diffusion coefficient.
*d* diameter; distance; (density).
d differential.
∂ partial differential.
*E* energy; (intrinsic energy); potential difference, especially electromotive force of voltaic cells.
*with subscript:* single electrode potential.
*e* electronic charge—charge equal and opposite in sign to that of an electron.
*e* quantity of electricity, especially electrostatic charge.
*with subscript:* single electrode potential.

e base of natural logarithms.
***F*** Faraday's constant.
*F* force; (free energy—Helmholtz).
F. farad; Fahrenheit.
*f* acceleration; activity coefficient, for molar concentration; partition function.
f function.
*G* thermodynamic potential, Gibbs function, free energy—G. N. Lewis.
***g*** acceleration due to gravity, standard value.
*g* acceleration due to gravity, as a variable; osmotic coefficient.
g. gram.
*H* enthalpy, total heat, heat content; magnetic field strength.
H. henry.
***h*** Planck's constant.
*h* height.
*I* moment of inertia; ionic strength; electric current; intensity of light.
*i* vapour pressure constant; van 't Hoff's factor.
***J*** mechanical equivalent of heat.
*J* gram-equivalent weight.
*K* chemical equilibrium constant; (compressibility).
$K_s$ solubility product.
K. Kelvin.
***k*** Boltzmann's constant.
*k* thermal conductivity; velocity constant of chemical reaction.
*L* latent heat per mol; self inductance; (solubility product).
*l* latent heat per g.; length; mean free path of molecules.
*with subscript:* equivalent ionic conductance, "mobility".
l. litre.
*M* molecular weight; mutual inductance; magnetic moment.
M. molar concentration.
***m*** rest mass of an electron.
*m* mass.
m. metre.
***N*** Avogadro's number.
*N* mol fraction.
N. normal concentration.
*n* number of mols.
*with subscript:* (transport number).
*with subscript:* refractive index.
*P* pressure.
[*P*] parachor.
*p* pressure.
*Q* quantity of electricity.
*q* heat entering a system.
***R*** gas constant per mol; Rydberg's constant.
*R* electrical resistance.
[*R*] *with subscript:* molecular refraction.
*r* radius; (specific resistance).
*with subscript:* specific refraction.
r. Röntgen unit.
*S* entropy.
*s* solubility; (surface area).
*T* temperature, on absolute Kelvin scale.
*with subscript:* transport number.
*t* time; (temperature—not on absolute scale).
*U* intrinsic energy.
*u* velocity component.
*with subscript:* velocity of ions.
*V* volume; potential, potential difference, including Volta potential.

v. volt.
$v$ volume; velocity; velocity component.
$W$ (work done by or on a system).
w. watt.
$w$ work done by or on a system; velocity component.
$X$ force component; potential gradient in electric field.
$x$ mol fraction.
$Y$ force component.
$Z$ force component; g.-equivalent weight; number of molecular collisions per second; atomic number.
$z$ valency of an ion.

$\alpha$ degree of electrolytic dissociation; angle of optical rotation.
$[\alpha]$ specific optical rotation.
$\Gamma$ surface concentration excess.
$\gamma$ ratio of specific heats; surface tension.
$\Delta$ increment.
$\delta$ very small increment.
$\epsilon$ dielectric constant; molar extinction coefficient.
$\zeta$ electrokinetic potential.
$\eta$ efficiency of any process; viscosity; electrolytic polarisation, overvoltage.
$\theta$ angle of contact; temperature—not on absolute scale.
$\kappa$ compressibility; specific conductance; magnetic susceptibility—volume.
$\Lambda$ equivalent conductance.
$\lambda$ wave length.
$\mu$ chemical potential; dipole moment; magnetic permeability.
*with subscript:* (refractive index).
$\mu$. micron.
$\nu$ frequency; wave number.
$\Pi$ pressure, especially osmotic pressure.
$\Pi$ product.
$\pi$ (electrolytic polarisation, overvoltage).
$\pi$ ratio of circumference to diameter.
$\rho$ density; specific resistance.
$\Sigma$ sum.
$\sigma$ diameter of molecules; (surface tension); (specific conductance).
$\tau$ time interval, especially half or mean life.
$\phi$ fluidity; electronic exit work function; magnetic flux.
$\Phi$ function.
$\chi$ magnetic susceptibility—mass.
$\psi$ wave function.
$\Omega$. ohm.
$\omega$ angular velocity; specific magnetic rotation.

# ERRATA.

## VOL., 1939.

| Page. | Line. | |
|---|---|---|
| 1849 | 4 | for "2 : 3-*Dimethyl*" read "2 : 4-*Dimethyl*." |

## VOL., 1942.

534 *The second formula for basseol should be* .

537 *In the figure the numbers* II *and* III *should be interchanged.*

543 20 *The oxidation of methyl siaresinolate by the Oppenhauer reagent* (*see* p. 541) *is as follows ;* Methyl siaresinolate (1 g.), aluminium *tert.*-butoxide (3·3 g.), *cyclo*hexanone (10 c.c.), and toluene (50 c.c.) were boiled for 18 hours, the mixture diluted with water and extracted with ether, the extract dried and evaporated, and the residue heated to 100° in a high vacuum. The residue crystallised from dilute acetone in plates, m. p. 214—215°, $[\alpha]_D$ + 57° (*c* = 1·75 in chloroform), giving a yellow colour with tetranitromethane (Found : C, 76·9; H, 10·1. $C_{31}H_{48}O_4$ requires C, 76·8; H, 10·0%).

544 23 *for* "$C_{29}H_{44}$" *read* "$C_{29}H_{46}$."

545 16* The *dehydro-ester* was prepared as follows : Methyl acetyldihydro-α-elemolate (700 mg.) was boiled for 16 hours with freshly sublimed selenium dioxide (350 mg.) in AnalaR acetic acid (42 c.c.). The solution was evaporated to dryness under reduced pressure, the residue dissolved in ether, and the solution washed with water, sodium hydroxide, again with water, dried, and evaporated. The residue was dissolved in benzene, and the solution percolated through a short column of alumina. The solid recovered on evaporation of the benzene solution crystallised from methyl alcohol in flattened needles (400 mg.), m. p. 128—129° (Found : C, 77·1, 77·4; H, 10·4, 1·02. $C_{33}H_{52}O_4$ requires C, 77·3; H, 10·2%). As the intensity of the light absorption was less than had been expected, the compound was subjected to a lengthy repurification by chromatographic adsorption in petroleum solution, but was recovered unchanged and behaved like a pure compound.

550 41 *for* "β-Elemolic acid" *read* "β-Elemonic acid."

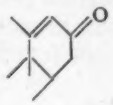
724 23 *for* "50°" *read* "5°."

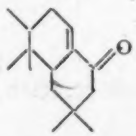
725 9 *for* "*NN'*-dimethyldiacridine" *read* "*NN'*-dimethyldiacridene."

19 *for* "*NN'*-Dimethyldiacridine" *read* "*NN'*-Dimethyldiacridene."

5* for "NN'-*Dimethyldiacridine*" read "NN'-*Dimethyldiacridene*."

741 22 for "*Helv. Chim. Acta*, 1942, **25**, 775" *read* "*Helv. Chim. Acta*, 1942, **25**, 1236."

*in formula* (III) *ring* D *should be* 

742 *formula* (VII) *should be* 

750 *add* H *in formula* (I).

752 30* *for* "-*d*-galactoside" *read* "*l*-galactoside."

39* *for* "←" *read* "→" *in bottom row of formulæ.*

## VOL., 1943.

52 34* *for* "below" *read* "above."

80 2 *for* "phosphoric oxide" *read* "phosphoric oxide (14 g.)."

* From bottom.

# PUBLICATIONS OF THE SOCIETY

With the exception of certain publications which are out of print, the following may be obtained from the General Secretary:

| | | Price to Fellows. £ s. d. | Price to Public. £ s. d. |
|---|---|---|---|
| Memoirs and Proceedings, 1841–1847 (3 vols.) | per vol. | 2 15 0 | 3 15 0 |
| Quarterly Journal, 1848–1861 (14 vols.) | per vol. | 2 15 0 | 3 15 0 |
| „ „ „ „ | per part | 5 6 | 7 6 |
| Journal, 1862–1870 | per vol. | 2 15 0 | 3 15 0 |
| „ (including Abstracts), 1871–1923 | per part | 5 6 | 7 6 |
| * „ 1924–1943 | | | |
| †British Chemical Abstracts "A" (Pure Chemistry), 1924–1937 | per vol. | 2 15 0 | 3 15 0 |
| | per part | 5 6 | 7 6 |
| †British Chemical and Physiological Abstracts "A," 1938–1943: | | | |
| A. I (General, Physical and Inorganic Chemistry) | per ann. | 1 0 0 | 2 15 0‖ |
| A. II (Organic Chemistry) | per ann. | 1 0 0 | 2 15 0‖ |
| A. III (Physiology and Biochemistry) | per ann. | 1 12 0 | 4 0 0‖ |
| A. I, A. II and A. III together | per ann. | 3 5 0 | 8 0 0‖ |
| †British Chemical Abstracts Annual Index, 1924–1937 | per copy | 7 0 | 11 0 |
| †Index to British Chemical and Physiological Abstracts, 1938, including "A" (Pure Chemistry and Physiology) and "B" (Applied Chemistry) | | 10 6 | 15 0 |
| 1939–1943 (A only) | | 10 6 | 12 6 |
| ‡Proceedings, 1885–1914 | per vol. | 7 6 | 7 6§ |
| „ „ | per part | 6 | 6§ |
| Annual Reports on the Progress of Chemistry: Vol. I (1904)—Vol. XL (1943) | per copy | 8 6 | 15 0 |
| Collective Index, Vol. I, 1841–1872 | per vol. | 2 0§ | 2 0§ |
| „ „ „ II, 1873–1882 | per vol. | 5 0§ | 5 0§ |
| „ „ „ III, 1883–1892 | per vol. | 7 6§ | 7 6§ |
| „ „ „ IV, 1893–1902 | per vol. | 10 0§ | 10 0§ |
| „ „ „ V, 1903–1912 | per vol. | 2 0 0§ | 2 10 0§ |
| „ „ „ VI, 1913–1922 | per vol. | 3 5 0§ | 5 0 0§ |
| †Decennial Index of British Chemical Abstracts, 1923–1932 | | 4 0 0§ | 8 0 0 |
| †Quinquennial Index of British Chemical Abstracts, 1933–1937 | | 4 0 0§ | 10 0 0 |
| (Obtainable from the Bureau of Chemical and Physiological Abstracts, 56, Victoria Street, S.W.1.) | | | |
| Jubilee Volume (giving history of the Chemical Society from 1841 to 1891) | | 2 6 | 2 6§ |
| Memorial Lectures, Vol. I, 1893–1900 (Reproduced) | | 9 0 | 10 6§ |
| „ „ „ II, 1901–1913 „ | | 7 0 | 8 0§ |
| „ „ „ III, 1914–1932 | | 5 0 | 6 0§ |
| Volume of Faraday Lectures | | 5 6 | 8 6§ |
| Portraits of Eminent Chemists, set of 8 | | 18 0 | 1 2 0§ |
| „ „ „ each | | 2 6 | 3 0§ |
| Tables of International Atomic Weights for 1941 (as recommended by the Committee on Atomic Weights of the Union Internationale de Chimie) | On cards: per doz. | 1 6 | 2 0§ |
| | per 50 | 5 6 | 7 6§ |
| | per 100 | 10 6 | 14 0§ |

* *As from January, 1924, the Abstracts were separated from the Transactions and were published independently.* † *Issued by the Bureau of Chemical and Physiological Abstracts.*

‡ *Included with Journal as from January, 1915.* § *Postage extra. All other publications post free.*

‖ *Including one copy of the Index in each case.*

# NOTICES TO AUTHORS OF PAPERS

1. All Scientific Communications for the Journal should be addressed to "The Secretaries, Chemical Society, Burlington House, W.1." Papers to be read before a meeting of the Society are selected by the Secretaries.

2. A paper is not normally considered for publication in the Journal unless at least one of the authors is a Fellow of the Society, but in exceptional circumstances the Council is prepared to consider papers submitted by non-Fellows.

3. An author must submit with every paper a signed form of declaration that to the best of his knowledge the paper does not contain any information that contravenes the Official Secrets Act.

4. An author engaged in any Government Department or similar body associated with the prosecution of the war must submit with his paper a written declaration from such Department or body that he has received authority to submit the paper for consideration for publication in the Journal.

5. All papers should be submitted in typescript in double-line spacing. Footnotes in papers add considerably to the cost of printing; authors are requested, therefore, not to use them unless necessary.

6. Every paper should be prefaced by a short summary setting forth briefly and in simple language the objects of the investigation, the results obtained and their bearing on chemical knowledge in general. The summary should be such as to enable any chemist to obtain a clear idea of what the investigation has achieved and should normally be from 50—250 words in length.

7. If he desires to do so, an author may send with the paper, for consideration by the Publication Committee, a confidential report by a Chemist of standing to whom the paper has been submitted.

8. The Publication Committee invites authors who publish series of related papers in the Journal to submit, at suitable intervals, papers reviewing their previously published work (suspended during the war).

9. The Society reserves the right to retain the Manuscript and illustrative drawings of all papers sent to it, and authors are therefore advised to keep copies. This right is not usually exercised in respect of illustrative drawings. When papers have been accepted for publication the authors are not at liberty, save by permission of the Council, to publish them elsewhere until such papers have appeared in the Journal of the Society. Papers which are retained by the Council after being judged unsuitable for publication in the Journal are deposited in the Archives of the Society.

10. Communications which have appeared in any other Journal shall not be published in the Journal of the Chemical Society unless this course is approved by a special vote of the Council.

11. The address to which proofs are to be sent should be written on every paper.

12. Authors resident overseas are requested to name agents in Britain to whom may be referred matters concerning their papers, including the correction of proofs, in order that delay in publication may be avoided.

13. Illustrations accompanying the papers must be carefully drawn, preferably **twice** the size of the finished block (max. width, 4½ inches), **in Indian ink,** on **smooth white Bristol board or paper.** Any illustration which exceeds four times the size of the finished block will be returned to the author for re-drawing to a smaller scale. Lettering on the drawings, whether on the margin or in the body of the drawing, must not be in ink but must be inserted *lightly in blue pencil.* Authors may, if they wish, submit in the first place clearly drawn pencil sketches instead of the completed diagrams, which, however, must be supplied before publication. Further information can be obtained from Dr. C. Smith, Staplefield Grange Farm, Haywards Heath, Sussex.

14. If any Author requires more than the number of reprints (without wrappers) allowed by the Society, namely, 10 plus 10 extra for each author in excess of one, or desires to receive his reprints in wrappers and is willing to pay the extra cost thereby involved, he should inform Dr. Smith at the time he sends in the corrected proof. Extra copies will be supplied at rates which can be obtained from the Editor.

# ADDITIONS TO THE LIBRARY OF THE CHEMICAL SOCIETY DURING THE YEAR 1943.

ABRAMSON, H. A., MOYER, L. S., and GORIN, M. H. Electrophoresis of proteins and the chemistry of cell surfaces. New York 1942. pp. 341. ill.

ADAMS, R. *See* ORGANIC REACTIONS.

ADDINALL, C. R. *See* MERCK & Co.

AIR MINISTRY. *Aeronautical Research Committee.* Reports and memoranda, No. 1901. Electrode potentials of metals. By A. H. TURNBULL and H. C. DAVIS. London 1942. pp. 17. ill.

ALLPORT, N. L. The chemistry and pharmacy of vegetable drugs. London 1943. pp. viii + 252. ill.

AMERICAN CHEMICAL SOCIETY. Chemical Abstracts. Vols. 34—36. Easton, Pa. 1940—42. (*For circulation.*)

AMERICAN PHARMACEUTICAL ASSOCIATION. The National Formulary. 7th edition. N.F. VII. Washington 1942. pp. viii + 690. (*Reference.*)

AMERICAN PUBLIC HEALTH ASSOCIATION and ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS. Standard methods for the examination of dairy products. 8th edition. New York 1941. pp. xvi + 288. ill.

AMERICAN SCIENTIFIC CONGRESS, VIII, Washington 1940. Proceedings. Vol. VII. Physical and chemical sciences. Washington 1942. pp. 448. ill. (*Reference.*)

AMERICAN SOCIETY FOR METALS. Controlled atmospheres. Cleveland 1942. pp. [iii] + 232. ill.

—— Powder metallurgy. Edited by J. WULFF. Cleveland 1942. pp. [viii] + 622. ill.

AMOR, A. J. The chemical aspects of silicosis. London 1942. pp. viii + 37.

ANDERSSON, B. Studien über die Co-Zymase als Aktivator bei enzymatischen Dehydrierungen. Stockholm 1938. pp. 136. ill.

ARAUJO, A. S. DE. *See* SILVA DE ARAUJO, A.

ARCHIVES OF BIOCHEMISTRY. Vol. I, etc. New York 1942 +. (*Reference.*)

ARENDS, G. *See* HAGERS Handbuch der pharmazeutischen Praxis.

ASSARSSON, G. Die Entstehungsbedingungen der hydratischen Verbindungen im System $CaO$–$Al_2O_3$–$H_2O$ (flüssig) und die Hydratisierung der Anhydrokalziumaluminate. (*Arsb. Sverig. geol. Unders.*, 1936, 30, No. 6.) pp. 202. ill.

ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS. *See* AMERICAN PUBLIC HEALTH ASSOCIATION.

ASSOCIATION OF SCIENTIFIC WORKERS. Planning of science. Report of proceedings of the open conference held at Caxton Hall, January 30th—31st, 1943. London 1943. pp. 127. ill.

ASTBURY, W. T. *See* IMPERIAL CHEMICAL INDUSTRIES, LTD.

ATKINSON, R. W. The chemistry of saké-brewing. (From the *Mem. Sci. Dept., Univ. Tokio*, 1881, No. 6.) pp. viii + 73. ill.

ATTFIELD, J. The origin, extension, and prevention of fires and the relation of mineral and vegetable oils, and other materials to fire. Four letters to "The Times" and an appendix. London 1872. pp. 31.

—— A pamphlet on the relation to each other of education and examination, especially with regard to pharmacy in Great Britain. 2nd edition. London 1882. pp. ix + 97.

BACHARACH, A. L. *See* ZECHMEISTER, L.

BAKER, T. T. Photographic emulsion technique. Boston 1941. pp. xii + 263. ill.

BARFF, F. Explanation of a method of preventing corrosion of iron and steel, as applied to naval and military purposes. London 1877. 10 pp. ill.

BATES, F. J. *See* UNITED STATES. *Department of Commerce.* National Bureau of Standards. Circular No. C440.

BAUMGARTNER, J. G. Canned foods: an introduction to their microbiology. London 1943. pp. viii + 157. ill.

BEALE, J. F. *See* THRESH, J. C.

BEARD, H. H. Creatine and creatinine metabolism. Brooklyn 1943. pp. x + 376.

BELL, D. J. Introduction to carbohydrate biochemistry. London 1940. pp. viii + 112. ill.

BENEDETTI-PICHLER, A. A. Introduction to the microtechnique of inorganic analysis. New York 1942. pp. viii + 302. ill.

BENNER, S. Über die Eigenschwingung freier Elektronen in einem konstanten Magnetfeld. Stockholm 1931. pp. 75. ill.

BENNETT, H. Substitutes: a handbook of substitutes and alternatives for chemicals, metals, fibers and other commercial products, including a plan for making a proper choice. Brooklyn 1943. pp. x + 225. (*Reference.*)

BENNION, E. B., and STEWART, J. Cake manufacture. 2nd edition. London 1943. pp. 264. ill.

BERNHEIM, F. The interaction of drugs and cell catalysts. Minneapolis 1942. Reprinted 1943. pp. iii + 86. ill.

BERNTHSEN, A. A textbook of organic chemistry. Revised by J. J. SUDBOROUGH. London 1941. Reprinted 1942. pp. xi + 1371.

BHAGAVANTAM, S. Scattering of light and the Raman effect. Brooklyn 1942. pp. x + 333. ill.

BICKNELL, F., and PRESCOTT, F. The vitamins in medicine. London 1942. pp. vii + 662. ill.

BIRINGUCCIO, V. The Pirotechnia. Venezia 1540. Translated from the Italian with an introduction and notes by C. S. SMITH and M. T. GNUDI. New York 1942. pp. xxvi + 476. ill.

BLOCH, M. A. *See* MAYER, A. W.

BOOHER, L. E. *See* UNITED STATES. *Department of Agriculture.* Circular No. 638.

BOYD, W. C. Fundamentals of immunology. New York 1943. pp. xv + 446. ill.

BRAUDE, F. Adhesives. Brooklyn 1943. pp. xiv + 154.

BRICK, R. M., and PHILLIPS, A. Structure and properties of alloys. New York 1942. pp. xiv + 227. ill.

BRITISH PLASTICS AND MOULDED PRODUCTS TRADER. Vol. 15, etc. London 1943 +. (*Reference.*)

BRITISH PLASTICS YEAR BOOK 1943. Bedford 1943. pp. 436. (*Reference.*)

BRITISH STANDARDS INSTITUTION. War emergency B.S. 76 : 1943. Tars for road purposes. pp. 12.

—— War emergency B.S. 381C : 1943. Colours for ready mixed paints. pp. 4. ill.

—— B.S. 410 : 1943. Test sieves. pp. 29. ill.

—— War emergency B.S. 929 : 1943. Ready mixed paints. pp. 11. ill.

—— War emergency B.S. 1070 : 1942. Black paint (tar base) for use on iron and steel. pp. 5. ill.

—— War emergency B.S. 1112 : 1943. Sizes of photographic paper. pp. 2.

—— War emergency B.S. 1122 : 1943. Painting of new public service road vehicles in war time. pp. 6.

—— War emergency B.S. 1124 : 1943. Household paint for exterior use. pp. 12. ill.

—— War emergency B.S. 1128 : 1943. Recommendations for primers for camouflage paints. pp. 14.

BROSSET, C. Elektrokemisk och Röntgènkristallografisk Undersökning av komplexa Aluminiumfluorider. Stockholm 1942. pp. 122. ill.

BRUNAUER, S. The adsorption of gases and vapors. Vol. I. Physical adsorption. Princeton 1943. pp. vii + 511. ill.

BUERGER, M. J. *X*-ray crystallography : an introduction to the investigation of crystals by their diffraction of monochromatic *X*-radiation. New York 1942. pp. xxii + 531. ill.

BUNBURY, H. M. *See* HEILBRON, I. M.

BURDON, R. S. Surface tension and the spreading of liquids. Cambridge 1940. pp. xii + 85. ill.

BURGESS, R. *See* GALLOWAY, L. D.

BURK, R. E., and GRUMMITT, O. [Editors.] The chemistry of large molecules. (Frontiers in Chemistry. Vol. I.) New York 1943. pp. xi + 313. ill.

BURSTRÖM, H. Über antagonistische Erscheinungen bei der Kationenaufnahme des Hafers. (From the *Svensk bot. Tidskr.*, 1934, 28.) ill.

BURTON, E. F., and KOHL, W. H. The electron microscope. New York 1942. pp. 233. ill.

CALVERT, F. C. Experiments on the oxidation of iron, with appendices. Manchester 1872. pp. 31.

CARVALHO DE MORAES BASTOS, W. Determinação quantitativa do aluminio; sua precipitação por meio da fenilhidrazina. Rio de Janeiro 1942. pp. 54.

CHEMICAL INDUSTRIES. 18th edition. Edited by L. IVANOVSZKY. London 1943. pp. xxiv + 360. ill. (*Reference.*)

CHERONIS, N. D. Semimicro and macro organic chemistry : a laboratory manual. New York 1942. pp. xiii + 388 [+ 41]. ill.

CHOLNOKY, L. *See* ZECHMEISTER, L.

CLANCEY, VERNON J. Chemistry and the aeroplane. London 1942. pp. 176. ill.

CLARKE, F. W. *See* UNITED STATES. *Bureau of Education.*

CLIFFORD, W. K. Atoms. (Lecture delivered in the Hulme Town Hall, Manchester.) London 1872. pp. [21].

CLOWES, F., and COLEMAN, J. B. Quantitative chemical analysis. 11th edition. London 1918. pp. xxiv + 580. ill.

COOK, A. H. *See* MAYER, F.

COPPER DEVELOPMENT ASSOCIATION. Copper alloy resistance materials. C. D. A. Publication No. 38. London 1943. pp. 43. ill.

CRAFTS, A. S. *See* ROBBINS, W. W.

CRODA LTD. Lanoline paints and compositions. British Patents 503,772, 505,482. Goole [1943]. pp. 16.

CROSSMAN & PAULIN. Cane sugar manure. Berwick-upon-Tweed 1879. pp. 27.

CURTMAN, L. J. Introduction to semimicro qualitative chemical analysis. New York 1942. pp. x + 377. ill.

DACK, G. M. Food poisoning. Chicago 1943. pp. xi + 138.

DAKE, H. C., and DE MENT, J. Ultra-violet light and its applications. Brooklyn 1942. pp. viii + 209. ill.

DAVIS, H. C. *See* AIR MINISTRY. *Aeronautical Research Committee.*

DEGERING, E. F. An outline of the chemistry of the carbohydrates. Cincinnati 1943. pp. viii + 474. ill.

DE MENT, J. *See* DAKE, H. C.

DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH. *National Physical Laboratory.* The technique of calibrating platinum thermocouples for use in liquid steel. London 1942. pp. 7. ill.

DEWBERRY, E. B. Food poisoning : its nature, history and causation. Measures for its prevention and control. London 1943. pp. viii + 187. ill.

DIXON, M. Manometric methods as applied to the measurement of cell respiration and other processes. 2nd edition. Cambridge 1943. pp. xiv + 155. ill.

DOAN, G. E., and MAHLA, E. M. The principles of physical metallurgy. 2nd edition. New York 1941. pp. xi + 388. ill.

DROZ, M. E. *See* MÜLLER, R. H.

DUNSTAN, A. E. *See* INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

DUTTON, W. S. Du Pont : one hundred and forty years. New York 1942. pp. x + 396. ill.

EGLOFF, G., HULLA, G., and KOMAREWSKY, V. I. Isomerization of pure hydrocarbons. New York 1942. pp. 499. ill.

EHRENSVÄRD, G. Über die Primärvorgänge bei Chemozeptorenbeeinflussung. (From the *Acta physiol. Scand.*, 1942, 3.) pp. 151. ill.

ELSDON, G. D. *See* RICHMOND, H. D.

EMELÉUS, H. J., and WATSON, H. B. Post-graduate lectures. London 1943. pp. 85. ill.

EPHRAIM, F. Inorganic chemistry. 4th English edition. By P. C. L. THORNE and E. R. ROBERTS. London 1943. pp. xii + 921. ill.

ERNSTRÖM, E. V. Über Amylasen. Studien über Stabilität, Hemmungserscheinungen und Reinigung. Stockholm 1930. pp. 210. ill.

EVANS, B. S., and HIGGS, D. G. Spot-tests for the identification of certain metallic coatings and of certain metals in bulk. Cambridge 1943. pp. [ii] + 24. (*Reference.*)

FARRIS, E. J. *See* GRIFFITH, J. Q.

FIELD, S., and WEILL, A. D. Electroplating: a survey of modern practice including the analysis of solutions. 4th edition. London 1943. pp. viii + 437. ill.

FITCH, W. K. Gas warfare: a monograph for instructors. London 1942. Reprinted 1943. pp. 103.

FORBES, D. On the chemistry of the primeval earth. (From the *Geol. Mag.*, 1867, 4.) pp. 14.

FORRESTER, C., and GILBERT, W. Some aspects of the chemical and mineral industries with special reference to wartime problems and post-war industrial development. (From the *Trans. Min. Geol. Met. Inst. India*, 1941, 37.)

FOSTER, W. Experiments on the composition of coal. (From the *Minutes of Proc. Inst. Civil Engineers*, 1884, 77.) pp. 23.

FOWLER, A. B. *See* HANNAH DAIRY RESEARCH INSTITUTE. Bulletin No. 8.

FRANKLAND, E. On the educational and commercial utility of chemistry. (Introductory lecture on the opening of Owens College, Manchester.) Manchester 1852. pp. [17.]

FREAR, D. E. H. Chemistry of insecticides and fungicides. New York 1942. pp. viii + 300. ill.

FRERICHS, G. *See* HAGERS Handbuch der pharmazeutischen Praxis.

FRITSMAN, E. H. *See* MENDELÉEV, D. I.

FUNKE, G. W. Untersuchungen über die Spektren von NH und $C_2H_2$ (Acetylen). Stockholm 1937. pp. 74. ill.

FURNAS, C. C. *See* ROGERS, A.

FUSON, R. C., and SNYDER, H. R. Organic chemistry. New York 1942. pp. viii + 506.

GALLOWAY, L. D., and BURGESS, R. Applied mycology and bacteriology. [2nd edition.] London 1940. pp. viii + 186. ill.

GARMAN, R. L. *See* MÜLLER, R. H.

GETTENS, R. J., and STOUT, G. L. Painting materials: a short encyclopedia. New York 1942. pp. vii + 333. ill. (*Reference.*)

GIBSONE, B. W. Chemical addenda: being a brief exposition of the salient features of modern chemistry, compiled chiefly from the papers of Brodie, Dalton, etc. London 1866. pp. 23.

GILBERT, W. *See* FORRESTER, C.

GNUDI, M. T. *See* BIRINGUCCIO, V.

GOLDSTEIN, B. I. Researches on the biochemistry of protein fibres. (Kateprina.) Kiev 1938. pp. 202. ill. [In Russian.]

GOPPELSROEDER, F. Premiers résultats des études sur la formation des matières colorantes par voie électro-chimique. Mulhouse 1881. pp. 24. ill.

GORE, G. On the relation of science to electroplate manufacturers. Part I. (From the *Popular Science Rev.*, 1862.) pp. 7.

GORIN, M. H. *See* ABRAMSON, H. A.

GRÄBE, C., and LIEBERMANN, C. Das künstliche Alizarin. (From the *Amtl. Ber. Wiener Weltausstellung*, 1873, 3.) pp. 38.

GRAHAM, T. [and others]. Reports on the successful application of methylated spirit . . . to various purposes in the arts, manufactures, and scientific research, in 1856; addressed to the Commissioners of Inland Revenue. London 1856. pp. 55.

GRIFFITH, J. Q., and FARRIS, E. J. [Editors.] The rat in laboratory investigation. Philadelphia 1942. pp. xvi + 488. ill.

GRUMMITT, O. *See* BURK, R. E.

GRUNDSTRÖM, B. Spektroskopische Untersuchungen über die Erdalkalihydride. Stockholm 1936. pp. 95. ill.

GRUSE, W. A., and STEVENS, D. R. The chemical technology of petroleum. 2nd edition. New York 1942. pp. xiv + 733. ill.

GSTIRNER, F. Chemisch-physikalische Vitaminbestimmungsmethoden für das chemische, physiologische und klinische Laboratorium. 2nd edition. Stuttgart 1940. pp. xii + 226. ill.

GUNTSCH, A. Das Bandenspektrum des Magnesiumhydrides. Åbo 1939. pp. 104. ill.

HAERING, D. W. Organic methods of scale and corrosion control. 5th edition. Chicago 1943. pp. 27. ill.

HAGERS Handbuch der pharmazeutischen Praxis, für Apotheker, Arzneimittelhersteller, Drogisten, Ärzte und Medizinalbeamte. Edited by G. FRERICHS, G. ARENDS and H. ZÖRNIG. 2 vols. Berlin 1938. pp. xii + 1573, vi + 1579. (*Reference.*)

HAGGARD, H. W. *See* HENDERSON, Y.

HALLIBURTON, W. D., and MCDOWELL, R. J. S. Handbook of physiology and biochemistry. 37th edition. London 1942. pp. x + 977. ill.

HANNAH DAIRY RESEARCH INSTITUTE. Bulletin No. 8. The production of artificially dried grass. By J. MCNAIR and A. B. FOWLER. Kirkhill 1942. pp. 111. ill.

HARCOURT, A. G. V. On some points in chemical nomenclature. (From the *Proc. Ashmolean Soc.* 1866, N.S. No. 1.) pp. 4.

—— Photometry by the pentane standard. (From the *J. Gas Lighting*, 1885.) pp. 4.

HARRIS, R. S. *See* VITAMINS AND HORMONES.

HARTZLER, E. R. *See* UNITED STATES. *Department of Agriculture.* Circular No. 638.

HASSLER, J. W. Active carbon, the modern purifier. [4th edition.] New York 1941. pp. vii + 159. ill.

HEDESTRAND, G. Studien über amphotere Elektrolyte. Lund 1932. pp. 134. ill.

HEILBRON, I. M., and BUNBURY, H. M. [Editors.] Dictionary of organic compounds. 2nd edition. Vol. 1. London 1943. pp. xvi + 1072. (*Reference.*)

HEILMEYER, L. Spectrophotometry in medicine: being the authorised translation of "Medizinische Spektrophotometrie." Translated by A. JORDAN and T. L. TIPPELL. London 1943. pp. xvi + 280. ill.

HEIMER, A. Die Bandenspektren des Wismuthydrids und -deutrids und der Kobalt- und Nickelhydride. Lund 1937. pp. 80. ill.

HEIMER, T. Die Bandenspektren der Hydride und Deutride des Kupfers und Goldes. Lund 1937. pp. 86. ill.

HELLSTRÖM, H. Spektrophotometrische Ergebnisse an biochemisch wichtigen Stoffgruppen. Stockholm 1938. pp. 148. ill.

HENDERSON, Y., and HAGGARD, H. W. Noxious gases and the principles of respiration influencing their action. 2nd edition. New York 1943. pp. 294. ill.

HEWSTON, E. M. *See* UNITED STATES. *Department of Agriculture.* Circular No. 638.

HIGGS, D. G. *See* EVANS, B. S.

HIMUS, G. W. Fuel testing: laboratory methods in fuel technology. 2nd edition. London 1942. pp. xvi + 288. ill.

HINDS, W. On some points in the chemistry and physiology of aquaria. (From the *Birmingham Med. Rev.*, 1878.) pp. 17.

HIRST, H. X-rays in research and industry. Melbourne 1942. pp. 96. ill.

HOPKIN & WILLIAMS, LTD. Organic reagents for metals and for certain acid radicals. 4th edition. London 1943. pp. 176. (*Reference.*)

HOU, T. P. Manufacture of soda. 2nd edition. pp. xviii + 590. ill.

HULLA, G. *See* EGLOFF, G.

IMPERIAL CHEMICAL INDUSTRIES, LTD. Textile fibres under the X-rays. By W. T. ASTBURY. London [1943]. pp. 53. ill.

INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND. Chemistry and the petroleum industry. By A. E. DUNSTAN. London 1942. pp. 48. ill.

—— Some notes on water treatment. By R. G. PELLY. 25th Streatfeild Memorial Lecture. London 1943. pp. 24. ill.

INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND. *See also* ROYAL INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

INTERNATIONAL ELECTRIC AND GAS EXHIBITION, 1882—83. A short account of coal gas: the organization of its supply, and its utilization for lighting and other purposes. London [1883]. pp. 32.

ISTANBUL, L'UNIVERSITÉ DE. Revue de la Faculté des Sciences. Sér. A & B. Vol. 6, Fasc. 3/4, etc. Istanbul 1941 +. (*Reference.*)

IVANOVSZKY, L. *See* CHEMICAL INDUSTRIES.

JORDAN, A. *See* HEILMEYER, L.

JUNGFLEISCH, E. On the preparation of lævotartaric acid. From the *Proc. Birmingham Phil. Soc.*, 1883, 3.)

KALICHEVSKY, V. A., and STAGNER, B. A. Chemical refining of petroleum: the action of various refining agents and chemicals on petroleum and its products. [2nd edition.] New York 1942. pp. 550. ill.

KARRER, P. Lehrbuch der organischen Chemie. 7th edition. Leipzig 1941. pp. xxiii + 1001. ill.

KLEIN, F. D., JUN. Process practices in the aircraft industry. New York 1942. pp. xii + 266. ill.

KNAVE, E. B. Über die Bandenspektren einiger Metallhydride. (From the *Nova Acta Soc. Sci. upsal.*, 1932, (4), 8.) pp. 98. ill.

KOHL, W. H. *See* BURTON, E. F.

KOLTHOFF, I. M., and SANDELL, E. B. Textbook of quantitative inorganic analysis. 2nd edition. New York 1943. pp. xvii + 794. ill.

KOMAREWSKY, V. I. *See* EGLOFF, G.

KURNAKOV, N. S. Introduction to physicochemical analysis. 4th edition. Moscow 1940. pp. 562. ill. [In Russian.]

LANGMUIR, I. *See* TAYLOR, H. S.

LAVINE, I. *See* ZIMMERMAN, O. T.

LAWES, SIR J. B. On the application of different manures to different crops, and on their proper distribution on the farm. [1861]. pp. 20.

—— Fertility. London 1881. pp. 70.

LAWRENCE, E. O. *See* TAYLOR, H. S.

LEACH, A. E. Food inspection and analysis. 2nd edition. London 1909. pp. xviii + 954. ill.

LE BRETON, E. Signification physiologique de l'oxydation de l'alcool éthylique dans l'organisme. Lons-le-Saunier 1936. pp. 258. ill.

LEWIS, W. B. Electrical counting: with special reference to counting alpha and beta particles. Cambridge 1942. pp. [viii] + 144. ill.

LINDE, J. O. Elektrische Widerstandseigenschaften der verdünnten Legierungen des Kupfers, Silbers und Goldes. Lund 1939. pp. 96. ill.

LINDHOLM, E. Über die Verbreiterung und Verschiebung von Spektrallinien: experimentelle und theoretische Beiträge. Uppsala 1942. pp. 94. ill.

LIVESEY, G. The purification of gas from sulphur compounds other than sulphuretted hydrogen. London 1876. pp. 12.

LLOYD, D. J. *See* ROYAL INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

LOESCHBRANDT, F. Bleaching of sulphate pulp. Translated by E. MARTIN. New York 1941. pp. 71. ill.

LOESECKE, H. W. VON. Outlines of food technology. New York 1942. pp. 505. ill.

LOPEZ DE AZCONA, J. M. Estudio geoquímico de las blendas. Madrid [1943.] pp. 15. ill.

MCADAMS, W. C. Heat transmission. 2nd edition. New York 1942. pp. xiv + 459. ill.

MCDOWELL, R. J. S. *See* HALLIBURTON, W. D.

MCINNES, D. A., and others. The ultracentrifuge. (From *Ann. N.Y. Acad. Sci.*, 1942, 43.) ill.

MACLEAN, I. S. The metabolism of fat. London 1943. pp. vi + 104.

MCNAIR, J. *See* HANNAH DAIRY RESEARCH INSTITUTE. Bulletin No. 8.

MACVICAR, J. G. The normal products of hepatic action. Part I. Glycogenic and fatty matters. Part II. Cholesterine, etc. (From the *Edinburgh Med. J.*, 1871.) pp. 16, 15.

—— On the cause of the prophylactic and therapeutic value of table salt, iodide of potassium, etc. (From the *Edinburgh Med. J.*, 1873.) pp. 11.

MACY, I. G. Nutrition and chemical growth in childhood. Vol. I. Evaluation. Springfield, 1942. pp. xxvi + 432. ill.

MAHLA, E. M. *See* DOAN, G. E.

MARTIN, E. *See* LOESCHBRANDT, F.

MASTERS, M. T., and GILBERT, J. H. Reports of experiments made in the gardens of the Royal Horti-

cultural Society at Chiswick in 1869, on the influence of various manures on different species of plants. (From the *Proc. R. Hort. Soc.*, 1870.) ill.

MAYER, A. W. Chemical technical dictionary. (German-English-French-Russian.) Vol. I. Translation under the direction of B. N. MENSCHUTKIN and M. A. BLOCH. Brooklyn 1942. pp. 872. (*Reference.*)

MAYER, F. The chemistry of natural coloring matters: the constitutions, properties, and biological relations of the important natural pigments. Translated and revised by A. H. COOK. New York 1943. pp. ii + 354.

MEDICAL RESEARCH COUNCIL. War memorandum No. 2. Notes on gas gangrene: prevention, diagnosis, treatment. London 1943. pp. 28.

—— War memorandum No. 10. The medical use of sulphonamides. London 1943. pp. 46.

MENDELÉEV, D. I. Literary remains. Vol. I. Edited by E. H. FRITSMAN. Leningrad 1938. pp. 132. ill. [In Russian.]

MENSCHUTKIN, B. N. *See* MAYER, A. W.

MERCK & Co. Alpha tocopherol (vitamin E). Annotated bibliography and supplement. Rahway 1941. pp. iv + 92, iv + 13.

—— Ascorbic acid in wound healing. Annotated bibliography. Rahway 1941. pp. iv + 15.

—— Biotin. Annotated bibliography. Rahway 1942. pp. ii + 49.

—— Nicotinic acid. Annotated bibliography and supplement. Rahway 1941. pp. ii + 130, ii + 19.

—— Pantothenic acid. Annotated bibliography and supplement. Rahway 1941. pp. ii + 50, ii + 7.

—— Physiologic activity and clinical use of ascorbic acid (vitamin C). Rahway 1941. pp. ii + 59.

—— Physiologic activity and clinical use of riboflavin (6, 7-dimethyl-9-[1′-*d*-ribityl] isoalloxazine). Rahway 1941. pp. ii + 44.

—— Physiologic activity and clinical use of thiamine hydrochloride [vitamin $B_1$]. Rahway 1941. pp. ii + 49.

—— Physiologic activity and experimental clinical use of pantothenic acid (calcium pantothenate dextrorotatory). Rahway 1941. pp. ii + 23.

—— Riboflavin. Annotated bibliography and supplements. Rahway 1941—42. pp. iv + 113, iv + 12, iv + 27.

—— The story of vitamin $B_1$. Compiled by C. R. ADDINALL. Revised edition. Rahway 1940. pp. 72. ill.

—— Vitamin $B_1$ (thiamine hydrochloride). Annotated bibliography and supplement. Rahway 1941. pp. iv + 140, iv + 31.

—— Vitamin $B_6$ (pyridoxine). Annotated bibliography and supplement. Rahway 1941. pp. ii + 64, ii + 11.

—— Vitamin K. 2-Methyl-naphthoquinone (vitamin K-active), vitamin $K_1$, vitamin $K_2$, other related substances. Annotated bibliography and supplement. Rahway 1941. pp. iv + 78, iv + 20.

MIKA, J. Die exakten Methoden der Mikromassanalyse. (Chem. Analyse, Vol. XLII.) Stuttgart 1939. pp. xii + 180. ill. (*Reference.*)

MILKAL LABORATORY. Dried milk. No. 1. General information. London [1924.] pp. 24.

MINISTRY OF SUPPLY. The raw materials guide. London 1942. pp. 75. (*Reference.*)

MITTER, M. N. Manufacture of disinfectants and antiseptics. 2nd edition. Calcutta [1941]. pp. viii + 146.

MODERN PLASTICS. Vol. 20, No. 10, etc. New York 1943 +. (*Reference.*)

MORRELL, R. S. [Editor]. Synthetic resins and allied plastics. 2nd edition. London 1943. pp. xii + 580. ill.

MOYER, L. S. *See* ABRAMSON, H. A.

MÜLLER, O. H. The polarographic method of analysis. Easton 1941. pp. vi + 114. ill.

MÜLLER, R. H., GARMAN, R. L., and DROZ, M. E. Experimental electronics. New York 1942. pp. xv + 330. ill.

NAIMAN, B. *See* RIEMAN, W.

NEUSS, J. D. *See* RIEMAN, W.

NEWTON, J., and WILSON, C. L. Metallurgy of copper. New York 1942. pp. viii + 518. ill.

NØRDISKE KEMIKERMØDE, V, København 1939. Forhandlinger. København 1940. pp. 264. ill. (*Reference.*)

NORDISKE KJEMIKERMØTE, IV, Oslo 1932. Forhandlinger. Oslo 1933. pp. 323. ill. (*Reference.*)

OLSSON, E. The band spectra of sulphur, selenium and tellurium. Åbo 1938. pp. 136. ill.

ORGANIC REACTIONS. Edited by R. ADAMS [and others]. Vol. I. New York 1942. pp. viii + 391. (*Reference.*)

OSEEN, C. W. *See* SCHEELE, C. W.

PEASE, R. N. Equilibrium and kinetics of gas reactions: an introduction to the quantum-statistical treatment of chemical processes. Princeton 1942. pp. ix + 236.

PELLY, R. G. *See* INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

PHILLIPS, A. *See* BRICK, R. M.

PICTET, A. Souvenirs et travaux d'un chimiste. Neuchatel 1941. pp. 228. ill.

PILAR, F. A. B., and SILVA DE ARAUJO, A. Considerações sobre as propriedades anti-detonantes do alcool e seu emprego como combustivel. Rio de Janeiro 1942. pp. 42. ill.

PRESCOTT, F. *See* BICKNELL, F.

QUAKER OATS CO. *Technical Division.* Furfural as a selective solvent. Chicago 1940. pp. 11. ill.

—— —— The furans: chemicals made from oat hulls. Chicago 1941. pp. 20.

RADLEY, J. A. Starch and its derivatives. 2nd edition. London 1943. pp. xii + 558. ill.

RANDALL, M., and YOUNG, L. E. Elementary physical chemistry. Berkeley 1942. pp. xiv + 455. ill.

RAYLEIGH, FOURTH BARON. The life of Sir J. J. Thomson, O.M. Cambridge 1942. pp. x + 299. ill.

RAYNOR, R. N. *See* ROBBINS, W. W.

RICHMOND, H. D. Dairy chemistry. 4th edition. By G. D. ELSDON and G. H. WALKER. London 1942. pp. viii + 472.

RIEGEL, E. R. Industrial chemistry. New York 1942. pp. 861. ill.

RIEMAN, W., NEUSS, J. D., and NAIMAN, B. Quantitative analysis: a theoretical approach. 2nd edition. New York 1942. pp. xi + 496. ill.

ROBBINS, W. W., CRAFTS, A. S., and RAYNOR, R. N. Weed control: a textbook and manual. New York 1942. pp. xi + 543. ill.

ROBERTS, E. R. *See* EPHRAIM, F.

ROBINSON, C. S. The recovery of vapors, with special reference to volatile solvents. New York 1942. pp. 273. ill.

ROBINSON, F. A. *See* ZECHMEISTER, L.

ROGERS, A. Industrial chemistry. 6th edition. Edited by C. C. FURNAS. 2 vols. New York 1942. pp. xiv + 878, viii, 879 to 1721. ill.

ROSENBERG, H. R. Chemistry and physiology of the vitamins. New York 1942. pp. xx + 674. ill.

ROYAL INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND. Lecture on leather. By D. J. LLOYD. London 1943. pp. 31. ill.

ROYAL INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND. *See, also* INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

RUKEYSER, M. Willard Gibbs. New York 1942. pp. xii + 465. ill.

RULE, H. G. *See* SCHMIDT, J.

RYDBERG, R. Über Neubildung und Zerfall zweiatomiger Moleküle von spektroskopischem Standpunkte aus. Stockholm 1934. pp. 75. ill.

SANDELL, E. B. *See* KOLTHOFF, I. M.

SCHEELE, C. W. Manuskript 1756—77. Interpreted by C. W. OSEEN. Stockholm 1942. pp. viii + 173.

SCHMIDT, J. A text-book of organic chemistry. 4th edition. English edition by H. G. RULE. London 1943. pp. xxvii + 923. ill.

SFIRAS, J. Cypress oil from Kenya. (From *Recherches*, 1939, 3.) ill.

SILLÉN, L. G. X-ray studies on oxides and oxyhalides of trivalent bismuth. Stockholm 1940. pp. 140. ill.

SILVA DE ARAUJO, A. *See* PILAR, F. A. B.

SMITH, C. S. *See* BIRINGUCCIO, V.

SMITH, G. An introduction to industrial mycology. 2nd edition. London 1942. pp. xii + 260. ill.

SMITH, G. F. Cerate oxidimetry: further applications in the use of cerium in volumetric analysis. Columbus 1942. pp. 123. ill.

SNELL, G. D. [Editor]. Biology of the laboratory mouse. Philadelphia 1941. pp. ix + 497. ill.

SNYDER, H. R. *See* FUSON, R. C.

SOBOTKA, H. The chemistry of the sterids. Baltimore 1938. pp. xiii + 634. ill.

SOCIETY OF CHEMICAL INDUSTRY. *Food Group*. Proceedings. Vol. I, etc. London 1938 +. (*Reference.*)

—— *Plastics Group*. Proceedings. Vol. I, etc. London 1939 +. (*Reference.*)

SOMERS, G. F. *See* SUMNER, J. B.

SPEAKMAN, J. C. An introduction to the modern theory of valency. 2nd edition. London 1943. pp. 159.

SPRENGEL, H. Sprengel's vacuum-pump. (Commonly called "Bunsen's pump.") 2nd edition. London 1882. pp. 12.

STAGNER, B. A. *See* KALICHEVSKY, V. A.

STENVINKEL, G. Das Bandenspektrum des Zinkhydrides: Störungen in den Bandenspektren zweiatomiger Moleküle. Stockholm 1936. pp. 96. ill.

STERN, K., and WILLHEIM, R. The biochemistry of malignant tumours. Brooklyn 1943. pp. xiv + 951.

STEVENS, D. R. *See* GRUSE, W. A.

STEWART, J. *See* BENNION, E. B.

STOURDZÉ, Y. E. As argilas descorantes e sua ativação: tecnologia, análises e apliçacões. Rio de Janeiro 1941. pp. 193.

STOUT, G. L. *See* GETTENS, R. J.

STRUTT, J. W. *See* RAYLEIGH, FOURTH BARON.

SUCKLING, E. V. *See* THRESH, J. C.

SUDBOROUGH, J. J. *See* BERNTHSEN, A.

SUMNER, J. B., and SOMERS, G. F. Chemistry and methods of enzymes. New York 1943. pp. xi + 365. ill.

SVENSSON, E. Die Bandenspektren des Cadmiumhydrides und -deutrides und deren Feinstruktur im Vergleich mit anderen Dublettspektren. Stockholm 1935. pp. 91. ill.

SWANK, E. E. The story of food preservation. [Pittsburgh] 1942. pp. 101. ill.

SWIETOSLAWSKI, W. Coke formation process and physico-chemical properties of coals. New York 1942. pp. viii + 145. ill.

TAYLOR, H. A. *See* TAYLOR, H. S.

TAYLOR, H. S., LAWRENCE, E. O., and LANGMUIR, I. Molecular films, the cyclotron, and the new biology. New Brunswick 1942. pp. vi + 95. ill.

TAYLOR, H. S., and TAYLOR, H. A. Elementary physical chemistry. 3rd edition. New York 1942. pp. xi + 551. ill.

TECNOQUIMICA. Vol. III. Buenos Aires 1943. (*Reference.*)

THIMANN, K. V. *See* VITAMINS AND HORMONES.

THOMPSON, M. DE KAY. The total and free energies of formation of the oxides of thirty-two metals. New York 1942. pp. 89.

THORÉN, F. Zur Kenntnis des katalytischen Zersetzung von Wasserstoffsuperoxyd mit kolloidalem Platin. Stockholm 1930. pp. 135. ill.

THORNE, P. C. L. *See* EPHRAIM, F.

THRESH, J. C., BEALE, J. F., and SUCKLING, E. V. The examination of waters and water supplies. 5th edition by E. V. SUCKLING. London 1943. pp. x + 849. ill.

TIPPELL, T. L. *See* HEILMEYER, L.

TURNBULL, A. H. *See* AIR MINISTRY. *Aeronautical Research Committee.*

UNION OF SOCIALIST SOVIET REPUBLICS. *Academy of Sciences*. Jubilee Session. Moscow 1943. pp. 249. ill. [In Russian.]

UNITED STATES. *Bureau of Education*. Circular of Information No. 6—1880. A report on the teaching of chemistry and physics in the United States, by F. W. CLARKE. Washington 1881. pp. 219.

—— *Department of Agriculture*. Circular No. 638. A compilation of the vitamin values of foods in relation to processing and other variants. By L. E. BOOHER, E. R. HARTZLER and E. M. HEWSTON. Washington 1942. pp. 244. (*Reference.*)

UNITED STATES. *Department of Commerce.* National Bureau of Standards. Circular No. C427. Synthetic rubbers: a review of their compositions, properties, and uses. By L. A. WOOD. Washington 1940. pp. 29.

—— —— —— Circular No. C440. Polarimetry, saccharimetry and the sugars. By F. J. BATES and associates. Washington 1942. pp. xx + 810. ill. 2 copies.

UNITED STATES PHARMACOPŒIAL CONVENTION. The pharmacopœia of the United States of America. 12th revision. Easton, Pa. 1942. pp. lxxxviii + 880. (*Reference.*)

VAN DYKE, H. B., and others. Protein hormones of the pituitary body. (From the *Ann. N.Y. Acad. Sci.*, 1943, **43**.) ill.

VITAMINS AND HORMONES: advances in research and applications. Vol. I. Edited by R. S. HARRIS and K. V. THIMANN. New York 1943. pp. xviii + 452. ill. (*Reference.*)

WALKER, C. H. Crystallography for routine analysis. (From the *Metropolitan-Vickers Gazette*, 1943, **20**.) ill.

WALKER, G. H. *See* RICHMOND, H. D.

WARREN, C. M. On a process of fractional condensation. (From the *Mem. Amer. Acad.* 1865, N.S. **9**.) ill.

WATSON, H. B. *See* EMELÉUS, H. J.

WEILL, A. D. *See* FIELD, S.

WEST, E. S. Physical chemistry for students of biochemistry and medicine. New York 1942. pp. xv + 368. ill.

WILLHEIM, R. *See* STERN, K.

WILLS, T. On the products of combustion. (A lecture delivered before the British Association of Gas Managers.) London 1878. pp. 12.

WILSON, C. L. *See* NEWTON, J.

WILSON, W. The cathode ray oscillograph in industry. London 1943. pp. xii + 150. ill.

WINTON, A. L., and WINTON, K. B. The structure and composition of foods. Vols. I—III. New York 1932—37. pp. xiv + 710, xiv + 904, xxv + 524. ill.

WINTON, K. B. *See* WINTON, A. L.

WIRTSCHAFTER, Z. T. Minerals in nutrition. New York 1942. pp. 175. ill.

WOOD, L. A. *See* UNITED STATES. *Department of Commerce.* National Bureau of Standards. Circular No. C427.

WROUGHT LIGHT ALLOYS DEVELOPMENT ASSOCIATION. Information Bulletin No. 2. Guide to the properties of wrought aluminium alloys. Birmingham 1942. pp. 28.

WULFF, J. *See* AMERICAN SOCIETY FOR METALS.

YARWOOD, J. High vacuum technique: theory, practice, industrial applications and properties of metals. London 1943. pp. viii + 106. ill.

YOUNG, L. E. *See* RANDALL, M.

ZECHMEISTER, L., and CHOLNOKY, L. Principles and practice of chromatography. Translated from the 2nd German edition by A. L. BACHARACH and F. A. ROBINSON. 2nd impression (corrected and with supplementary bibliography). London 1943. pp. xvi + 378. ill.

ZIMMERMAN, O. T., and LAVINE, I. Chemical engineering laboratory equipment: design, construction, operation. Dover, N.H. 1943. pp. xi + 530. ill.

ZÖRNIG, H. *See* HAGERS Handbuch der pharmazeutischen Praxis.

PRINTED IN GREAT BRITAIN BY
RICHARD CLAY AND COMPANY, LTD.,
BUNGAY, SUFFOLK.